THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF CERTAIN MOLECULES

(Four spin systems and aqueous electrolytes)

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ABSTRACT OF THE THESIS ENTITLED "THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF CERTAIN MOLECULES."

In Chapter I of the thesis, a general introduction to the work presented in the other Chapters, and a description of the experimental method employed, are given. In addition, the basic theory involved in the analysis of spectra is briefly described. The Chapter is written with a view to provide an adequate general background to the work done, and the principles and notation presented here have been freely used in the rest of the Chapters.

Chapter II deals with the H^1 and F^{19} resonance spectra of 1-fluoro, 2,4-dinitrobenzene. This molecule is an unsymmetrical four spin system of the type ABCX. As the spectrum of one of the protons of this molecule is well separated from that of the other two, the secular equation for this system is completely solved in the first order approximation. The analysis, carried out on this basis, yields the values of all the parameters involved satisfactorily. The possibility, of determining the relative signs of some of the coupling constants in this type of spectra, is pointed out, and on this basis, it is found that the ortho & meta H-F coupling constants are of the same sign as the ortho & para H-H coupling

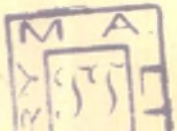
constants. The analysis is further refined by second order perturbation calculations, and more accurate values of the parameters are obtained.

In Chapter III, the work done on the proton resonance spectra of p-bromochlorobenzene, p-chlorotoluene and p-chloroiodobenzene, is described. The spectra of a number of p-disubstituted benzenes were studied earlier, but the analysis was done by making certain simplifying assumptions, and all the parameters are not determined. A method is proposed here to analyse this type of spectra (A_2B_2 type) without making these assumptions. The spectra of the above-mentioned molecules are, therefore, reinvestigated as examples of this method, and all the parameters have been determined.

Chapter IV consists of the study of proton resonance spectra of α, β & γ picolines. The spectra of ring protons in these molecules, which belong to the classes ABCX, ABXY and A_2X_2 respectively, are analysed to determine all the parameters involved.

While analysing the spectra in Chapters II, III & IV an attempt has been made to find some systematic features of the spectra, which will be of help in reducing the trial and error calculations, that are necessary in performing these analyses.

Studies on Cl^{35} resonance shifts in aqueous solutions of alkali chlorides and alkaline earth chlorides, and F^{19} resonance shifts in aqueous solutions of some alkali fluorides, form the second part of the thesis and are presented in Chapter V. These shifts are measured at various concentrations, and the results obtained show several interesting features which are qualitatively discussed in the light of the theories of chemical shifts and the solvent ion interactions in these solutions.



Certified that the work described in this thesis is the original work of Mr. B. D. Nageswara Rao, done under my supervision.

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C O N T E N T S.

CONTENTS (Contd.)

P R E F A C E

The High Resolution Nuclear Magnetic Resonance technique has, in recent years, acquired considerable importance as a useful method for investigating a variety of interesting problems associated with molecular electronic structure. The method essentially consists of the determination of the Chemical shifts and the spin-spin coupling constants, which represent the influence of the electronic distribution in the molecule, on the magnetic resonance of the nucleus of interest. These interactions give rise to complicated resonance spectra, in many cases, and detailed procedures have to be followed to analyze these spectra and obtain the parameters.

The work presented in this thesis may broadly be divided into two parts. The first part, which forms most of the work (Chapters II, III & IV), deals with the analysis of complicated spectra arising due to four spin systems. The second part of the thesis (Chapter V) concerns with the studies on negative ion resonance shifts in some aqueous electrolytes.

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All the work presented here is done in the Microwave and Radiofrequency Laboratory of the physics department, Muslim University, Aligarh, under the supervision of Dr. Putcha Venkateswarlu.

It gives me great pleasure to record here my indebtedness to Dr. Putcha Venkateswarlu for his excellant guidance and constant encouragement throughout.

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Sincere thanks are due to Dr. H. Sripathi Rao, Central Fuel Research Institute, Jealgora, for providing us with the samples of α, β and γ picolines worked in the present experiments. I wish to express my appreciation of the work done to me by the workshop and the glass-blowing sections of the physics department. I am very much grateful to several colleagues and friends in the department, especiall Messrs. K.V.L.N.Sastry, A.S.Rajan, R.P.Saxena, Y.V.Rao and D.R.Rao for their helpful cooperation and encouragement.

B. A. Nageswara Rao

CHAPTER I.

INTRODUCTION AND EXPERIMENTAL METHOD

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(i) General Introduction:

The Nuclear Magnetic Resonance (NMR) signals of most liquids exhibit a fine structure arising primarily due to two important effects associated with the electronic distribution in molecules viz., the chemical shift and the indirect spin-spin interaction between nuclei* (1-6). The chemical shifts represent variations in the electronic environment of the nuclei of interest at different non-equivalent sites in the molecule, and thus provide a sensitive method for observing slight and subtle changes in the electronic distribution. The spin-spin interaction is due to coupling of the different nuclear spins in the molecule through the bonding electrons. Though much work has not yet been done on the interpretation of these coupling constants in terms of molecular electronic distribution, some of the recent studies (7-10) have clearly shown that a good deal of information can be derived from an extensive study

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* References 1-4 deal with the subject of Nuclear Magnetic Resonance in bulk matter, in general, while references 5 and 6 deal with the phenomena associated with nuclear magnetism in liquids and are therefore more closely connected with the work described here.

of these coupling constants and their signs. The analyses of high resolution NMR spectra for accurate determination of these parameters, in molecules with varying degrees of bonding, forms an essential prerequisite for the more important aspect of deriving information from them. The work presented in this thesis mostly deals with the analyses of complex spectra.

When the chemical shifts between the different interacting nuclei are large compared to their mutual spin-spin interaction energy (this condition is easily satisfied if the interacting nuclei belong to different species) the high resolution spectrum shows several features of regularity and follows some simple rules (11-14) with which the parameters can be determined. But when the chemical shifts are of the same order of magnitude as the spin coupling constants, the spectrum becomes a complex and irregular multiplet and some detailed methods (12, 14, 15) have to be followed to analyze the spectra and derive the parameters. Though it is in principle possible to circumvent this difficulty by working at high magnetic fields, because the chemical shift is directly proportional to the static magnetic field, whereas the spin-spin interaction is independent of it, it is not often realized in practice as an upper limit is set, to the static magnetic field applied, by the requirements of stability and resolution. Further, it is always possible to have cases, even at very high static magnetic fields, where the

chemical shifts are still of the same order as the coupling constants involved. The general method of theoretical calculation of these spectra, where no restriction is placed on the relative values of the chemical shifts and the coupling constants, was given by McConnell, McLean and Reilly (16). The method is very much similar to the traditional methods, adapted in other branches of spectroscopy, of repeated solution of the quantum mechanical eigenvalue problem until the parameters chosen give a satisfactory agreement with the observed spectrum.

As this method has been used as the basis for the analysis of all the spectra in Chapters II, III & IV, it will be described here briefly, and the principles and notation presented below are freely used in these chapters.

(ii) Basic Theory of Analysis:

The "high resolution" Hamiltonian $\mathcal{H}$ for a system of 'p' interacting spins may be written as

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} \quad \ldots \quad (I.1)$$

where $$\mathcal{H}^{(0)} = \sum_{i=1}^{p} \nu_i I_{zi} \quad \ldots \quad (I.2)$$

and $$\mathcal{H}^{(1)} = \sum_{i<j} J_{ij} \vec{I}_i \cdot \vec{I}_j \quad \ldots \quad (I.3)$$

In these equations $\mathcal{H}^{(0)}$ represents the interaction of all the spins with the static magnetic field (chemical shift part). $\nu_i = \gamma_i H_{oi}$ where γ_i is the gyromagnetic ratio of the

i th nucleus at whose site the static magnetic field has the value H_{oi} . The direction of H_o is here taken as the negative z direction. $\mathcal{H}^{(1)}$ represents the spin-spin interactions between all the spins in the molecule. $\vec{I}_i$ is the spin angular momentum vector of the i th nucleus, and I_{xi}, I_{yi} & I_{zi} are its components along the coordinate axes. J_{ij} is the spin coupling constant between the nuclei i and j . Here the energies are all expressed in cycles per second to facilitate comparison with experimental spectra. In the absence of dynamic processes (17) which modify the observed spectra, and when the molecular motions in the liquid are rapid enough for the direct dipole-dipole interactions to be neglected, the above form of the Hamiltonian is expected (11,18,19) to represent faithfully all the observed features of high resolution NMR spectra.

Let ϕ°_{q} and ϕ_{q} be the eigenfunctions of $\mathcal{H}^{(o)}$ and $\mathcal{H}$ respectively, and E°_{q} and E_{q} the corresponding eigen-energies. The zero order eigenfunctions ϕ°_{q} then represent the stationary states in the absence of the term $\mathcal{H}^{(1)}$ in Eq. (I.1). The number of possible states are 2^p, if all the interacting nuclei are of spin $\frac{1}{2}$*, as is generally the

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* Extension of this method to nuclei with spin greater than $\frac{1}{2}$ is straightforward, but in practice such spectra are not generally encountered as they are vitiated by quadrupole effects.

case. Now the problem is to determine suitable linear combinations of ϕ_q° which diagonalize the matrix of the of the complete Hamiltonian $\mathcal{H}$. The corresponding eigenvalues E_q are given by the solution of the secular equation.

$$\left| \mathcal{H}_{mn} - E\, \delta_{mn} \right| = 0 \qquad \ldots \qquad (I.4)$$

where $\mathcal{H}_{mn} = (\phi_m^\circ | \mathcal{H} | \phi_n^\circ)$ and $\delta_{mn} = 1$ if $m=n$ and $\delta_{mn} = 0$ if $m \neq n$. The exact eigenfunctions ϕ_q are given by

$$\phi_q = \sum_m a_{qm}\, \phi_m^\circ \qquad \ldots \qquad (I.5)$$

where the coefficients a_{qm} are given by the set of linear equations

$$\sum_n \mathcal{H}_{mn}\, a_{qn} = E_q\, a_{qm} \qquad \ldots \qquad (I.6)$$

the solution of which yields the ratios of these coefficients. And the exact values are determined by the condition that the functions φ_q should be normalized, i.e.,

$$\sum_m a_{qm}^*\, a_{qm} = 1 \qquad \ldots \qquad (I.7)$$

The secular equation (1.4) is of the order 2^p, but with an appropriate choice of the zero order spin functions, this can be factored into several equations of lower order. The method of choosing these functions is described in detail by several authors (5,16,20) and shall be omitted here. The secular equation first factors into (p+1) separate equations corresponding to all the possible values of F_z the total spin component in the z direction.

$$F_z = \sum_i I_{zi} \qquad \ldots \qquad (I.8)$$

Further factorization of these equations results, if the molecule contains interacting nuclei of more than one species, as the off-diagonal matrix elements between states corresponding to different values of the z component of the total spin of any of the different nuclear spiecies can be taken as zero, to a high degree of approximation. The same argument can be applied, though to a less degree of approximation, to nuclei of the same species, where $|\nu_i - \nu_j| \gg J_{ij}$. Even in cases where this condition is not completely valid this factorization can be carried out in order to obtain approximate solutions of the energy values, which can be employed later as a starting point for more valid and rigorous approximations (21).

The problem is further simplified if the molecule under consideration possesses elements of symmetry. This has been realised by McConnell et.al.(16) themselves, and is later treated more exhaustively by Wilson (22). The zero order eigenfunctions then fall into symmetric and antisymmetric classes, and no mixing occurs between states belonging to different classes.

Once the secular equation (I-4) is completely solved, all the transition energies can be readily obtained by using the well known selection rule

$$\Delta F_z = \pm 1 \qquad \ldots \qquad (I.9)$$

In the case of symmetrical molecules, there is an additional selection rule by which transitions are allowed only between states of the same symmetry.

The ~~reduction~~ intensity of a transition between states corresponding to ϕ_m and ϕ_n is proportional to

$$\left[\left(\phi_m \left| \sum_i I_{xi} \right| \phi_n \right) \right]^2 \qquad \ldots \qquad (I.10)$$

and it can be calculated for all the transitions, if the exact eigenfunctions ϕ_m are evaluated by means of Eqns. (I.5), (I.6) & (I.7).

Several workers (5,16,20,23) have summarized convenient rules for evaluating the matrix elements involved in the above calculation of these theoretical spectra.

(iii) Spectra of Four Spin Systems:

The method described in the previous section cannot be applied easily to all cases, as it is difficult (though, in principle, not impossible) to derive explicit expressions for the transition energies in terms of the parameters, if the order of the subdeterminents is more than two. This condition is always satisfied if the number of interacting spins is only two (AB or AX type*). But the

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* The classification of spectra into different types, is done in accordance with the notation developed by Bernstein et.al. (5,20).

spectra of molecules containing more than two spins are of special interest as seen below.

Recent theoretical work (7,24,26) has shown that a knowledge of the signs of the coupling constants is of considerable importance. In order to determine these signs it is necessary that the number of interacting nuclei are at least three (14,27). It is to be noted, however, that only relative signs of coupling constants can be determined in NMR experiments, as the sign of the 2nd term in Eq. (I.1) is arbitrary. (A positive sign of J_{ij} in the form of $\mathcal{H}$ in Eqn. (I.1) corresponds to a preferred antiparallel correlation of the interacting spins i and j). But the theoretical analyses (24,25,26,28,29) have shown that H-H coupling constants are almost definitely positive, if they are greater* than a few cycles per second. Basing on this, the absolute signs of the coupling constants can be determined, if the relative signs are known. From this point of view, therefore, the spectra of three or more strongly coupled spins are of considerable current interest. Further, as was pointed out by Fessenden and Waugh (32) it is not yet correctly known whether the form of Hamiltonian in Eq. (I.1) represents the problem, adequately, when the number of interacting spins are large, as it is possible

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* Several workers (8,21,30,31) have recently obtained results which definitely yield negative values of the order a few cps. for some of the H-H coupling constants in vinyl protons.

that interactions of the type $\vec{I}_i \cdot (\vec{I}_j \times \vec{I}_k)$ might occur in these cases. But it may be mentioned that the results on the many spin spectra, analyzed so far, did not indicate the presence of any such interactions.

The spectra of these systems are usually complex and one often encounters determinents of order 3 or more to solve for the energy levels in terms of the many parameters*. The complexity of the spectrum is considerably reduced if ths molecule possesses symmetry; but the spectra of symmetrical molecules are usually insensitive to the signs of the coupling constants. On the other hand the spectra become rapidly complicated as the symmetry is reduced or when the number of nuclei is increased.** Some useful simplification can, of course, be obtained in cases where the condition $|\nu_i - \nu_j| \gg J_{ij}$ is satisfied. However, it will always be helpful if certain systematic features of the spectra could be found, though finally a good deal

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* If there are 'n' nuclei in the system, there will be (n-1) chemical shifts and n(n-1)/2 spin coupling constants to be determined from the analysis.

** This can be seen from the fact that an AB spectrum consists of 4 transitions, while there are 15 transitions in an ABC spectrum, and 56 in ABCD spectrum. If the four spin system has symmetry and falls in the class A_2B_2, only 24 transitions occur symmetrically about the center of the spectrum, so that only twelve lines need be identified for the analysis.

of trial and error calculation is to be done to assign all the transitions to the lines observed in the experimental spectrum.

Spectra of a number of three-spin systems, which are the simplest among the complex spectra, were studied recently by several workers (20,32,33) and the principles developed in these analyses are of much help in dealing with the more complicated cases of four and five spin spectra. In the present work, seven four spin spectra which fall into ABCX, ABXY, A_2B_2 and A_2X_2 classes* are analyzed and all the parameters are determined. The basic theory for A_2X_2(5,16) and A_2B_2(5,34) spectra was already given earlier, and it is applied to the specific cases studied. For the ABCX and ABXY systems the detailed theoretical calculations are performed.

(iv) Aqueous Electrolytes:

Chemical shift determinations have proved to be very useful in studying small variations in electronic environment of nuclei in a direct and simple manner (37-41). In the present work Cl^{35} resonance shifts in aqueous solutions of alkali chlorides and alkaline earth chlorides

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* Four spin systems belonging to the class ABX_2 have been recently studied by other workers (35,36).

and F^{19} resonance shifts in aqueous solutions of some alkali fluorides are measured. The work is done at various concentrations and the results obtained show some interesting features, which are discussed qualitatively in the light of the theories of chemical shifts and the solvent ion interactions in these solutions.

(v) Experimental:

All the spectra presented in this thesis are obtained on a Varian V-4300 B NMR Spectrometer, using a 12" electromagnet. Full details regarding the equipment and the accessories are published by the Varian Associates (42). The power supply for the magnet has voltage and current regulation, and the drifts in the field, occuring due to temperature variations etc., are compensated by a "Super Stabilizer" (42). The overall stability and homogeneity of the static magnetic field is usually better than 1 part in 10^7.* The spectrometer essentially consists of fixed frequency transmitter and receiver units with the

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* The homogeneity of the magnetic field can be improved considerably by adapting a cycling procedure (see Varian Associates' Instruction Manual). This procedure is absolutely essential for proton and fluorine resonance experiments as the lines in these spectra are very sharp, but need not be followed when the broad lines like those of Cl^{35} resonance are studied.

associated probe, and a sweep unit providing for variable sweep field of adjustable frequency. Two fixed frequency RF units are available in our set up, at operating frequencies of 3.6 Mc/Sec., and 40 Mc/Sec. The former is used for Cl^{35} resonance experiments, where as the latter for H^{1} and F^{19} resonance studies. The frequency stability of the RF unit is about 1 part in a million per hour. The spectrometer is also equipped with the "Sample Spinner" (42), which reduces the line widths and enhances the amplitudes of the lines. With this arrangement, the contribution to the line widths from magnetic field inhomogeneities is greatly reduced. The sample spinning technique, however, cannot be used with 3.6 Mc/Sec. unit (42).

The value of the static magnetic field for Cl^{35} resonance studies at 3.6 Mc/Sec. is about 8627 gauss, while for H^{1} and F^{19} resonance experiments at 40 Mc/Sec. the values are about 9395 and 10,000 gauss respectively.

A Dumont Model 304-AR Oscilloscope is used for visual observation of the resonances and a Sanborn Model 151-100A Recorder is employed for recording them. For recording a "Slow Sweep Unit" (42) is provided along with the Super Stabilizer with which the magnetic field can be varied either way, linearly, at a slow and variable rate.

The measurements are all done by the side band technique (43), using Hewlett-Packard Model 200B. Audio Oscillator to modulate the sweep voltage. The frequency of the Audio Oscillator is accurately determined by calibrating with the proton resonance spectrum of ethanol at 40 Mc/Sec. The error involved in this determination is not more than $\pm$ 2 cps.

When there are a large number of closely spaced lines, it is often found convenient to first determine by the side band method the mms separation between two prominent lines in the spectrum. Later, the positions of all other lines are determined on a spectrum taken at a larger dispersion, by linear interpolation. This method does not bring in any errors, as the recorder chart is driven by a synchronous motor, and the variation of the magnetic field is usually linear, when it is done with a slow sweep unit.

It is not usually possible to separate the several factors that contribute to the errors in the determination of the line positions. So the measurements are done generally, on at least ten spectra, and the standard deviations of the measurements of individual lines are taken as precision indexes. The standard deviation may again vary from line to line (It will be usually greater

if any overlapping of lines occurs) and the limits of this variation are given for measurements on each molecule. The mean of these limits may be taken to represent, approximately, the error involved in the measurements.

In all the proton resonance experiments the Sample Spinner is used. The sample tubes are about 5mm. in diameter (outer), and about 15cm. in length.

All the measurements reported in this thesis, are done at room temperature.

Further experimental details concerning specific cases are given at appropriate places in the thesis.

REFERENCES

1. Andrew. E. R., "Nuclear Magnetic Resonance", Cambridge University Press, New York, (1955).
2. Shoolery, J. N., and Weaver. H. E., Ann. Rev. Phys. Chem. 6, 433, (1955).
3. Gutowsky. H. S., Discussions of Faraday Society, 19, 246,(1955).
4. Pake. G. E., "Nuclear Magnetic Resonance" in "Solid State Physics", Vol. 2, Academic Press Inc., New York, (1956).
5. Pople. J. A., Schneider. W. G., and Bernstein. H. J., "High Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., New York, (1959).
6. Powles. J. G., Reports on Progress of Physics, 22, 433,(1959).
7. Williams. G. A., and Gutowsky. H. S., J. Chem. Phys., 30, 717, (1959).
8. Gutowsky. H. S., Karplus. M. and Grant. D. M., J. Chem. Phys. 31, 1278, (1959).
9. Muller. N. and Pritchard. D. E., J. Chem. Phys. 31, 768, (1959).
10. Muller. N. and Pritchard. D. E., J. Chem. Phys. 31, 1471, (1959).
11. Gutowsky. H. S., McCall. D. W. and Slichter. C. P., J. Chem. Phys. 21, 279, (1953).

12. Hahn. E. L. and Maxwell. D. E., Phys. Rev. 88, 1070, (1952).
13. Arnold. J. T., Phys. Rev. 102, 136 (1956).
14. Anderson. W. A., Phys. Rev. 102, 151,(1956).
15. Bannerjee. M. K., Das. T. P. and Saha. A. K., Proc. Roy. Soc. (London), 226A, 490, (1954).
16. McConnell. H. M., McLean. A. D. and Reilly. C. A., J. Chem. Phys. 23, 1152, (1955).
17. Gutowsky. H. S. and Holm. C. H., J. Chem. Phys. 25, 1228, (1956).
18. Ramsey. N. F. and Purcell. E. M., Phys. Rev. 85, 143, (1952).
19. Ramsey. N. F., Phys. Rev. 91, 303, (1953).
20. Bernstein. H. J., Pople. J. A. and Schneider. W. G. Can. J. Chem. 35, 65 (1957).
21. Fessenden. R. W. and Waugh. J. S., J. Chem. Phys. 30, 944 (1959).
22. Wilson. E. B., Jr., J. Chem. Phys., 27, 60, (1957).
23. Corin. P. L., J. Chem. Phys. 29, 682, (1958).
24. Karplus. M. and Anderson. D. H., J. Chem. Phys. 30, 6, (1959).
25. Karplus. M., J. Chem. Phys. 30, 11, (1959).
26. McConnell. H. M., J. Chem. Phys. 30, 126, (1959).
27. Williams. G. A. and Gutowsky. H. S., J. Chem. Phys. 25, 1288, (1956).

28. McConnell. H. M., J. Chem. Phys. 24, 460, (1956).

29. Karplus. M., Anderson. D. H., Farrar. T. C. and Gutowsky. H. S., J. Chem. Phys. 27, 597, (1957).

30. Alexander. S., J. Chem. Phys. 28, 358, (1958).

31. Banwell. C. N., Cohen. A. D., Sheppard. N., and Turner. J. J., Proc. Chem. Soc., 266, (1959).

32. Fessenden. R. W. and Waugh. J. S., J. Chem. Phys. 31, 996, (1959).

33. Gutowsky. H. S., Holm. C. H., Saika. A. and Williams. G. A., J. Am. Chem. Soc. 79, 4596, (1957).

34. Pople. J. A., Schneider. W. G. and Bernstein. H. J., Can. J. Chem. 35, 1060, (1957).

35. Mortimer. F. S., J. Mol. Spectroscopy. 3, 355, (1959).

36. Cohen. A. D., and Sheppard. N., Proc. Roy. Soc. (London), 252A, 488, (1959).

37. Gutowsky. H. S. and Hoffman. C. J., J. Chem. Phys. 19, 1259 (1951).

38. Gutowsky. H. S., McCall. D. W., McGarvey. B. R. and Meyer. L. H., J. Am. Chem. Soc. 74, 4809, (1952).

39. Meyer. L. H. and Gutowsky. H. S., J. Phys. Chem. 57, 481, (1953).

40. Meyer. L. H., Saika. A. and Gutowsky. H. S., J. Am. Chem. Soc. 75, 4567, (1953).

41. Gutowsky. H. S. and McCall. D. W., J.Chem.Phys.22,162(1954).

42. Varian Associates, Technical Information Bulletins.

43. Arnold.J.T. and Packard.M.E., J.Chem.Phys.19, 1608 (1951).

CHAPTER II.

THE H^1 AND F^{19} RESONANCE SPECTRA OF 1-FLUORO, 2,4-DINITROBENZENE

THE H^1 AND F^{19} RESONANCE SPECTRA OF 1-FLUORO, 2,4-DINITRO BENZENE

A B S T R A C T

High resolution H^1 and F^{19} nuclear magnetic resonance spectra of 1-fluoro, 2,4-dinitrobenzene are obtained and analyzed to determine all the parameters involved. As the spectrum of one of the protons is well separated from that of the other two, the secular equation has been solved in the first approximation. The analysis gives the following coupling constants: $J_o^{HH} = 8.65 \pm 0.3$ cps., $J_m^{HH} = 2.85 \pm 0.2$ cps., $J_p^{HH} = 0.65 \pm 0.3$ cps., $J_o^{HF} = 10.35 \pm 0.2$ cps., and the two meta H-F coupling constants were found to be considerably different being 6.45 ± 0.3 cps., and 3.85 ± 0.3 cps. It has been found that the ortho and meta H-F coupling constants have the same sign as the ortho and para H-H coupling constants.

The analysis is further refined by second order perturbation calculations, and more accurate values of the chemical shifts involved are obtained. The values of the coupling constants are not significantly affected by this refinement.

(i) Introduction:

Considerable amount of work (1-10) has been done recently on the spin-spin coupling constants in substituted benzenes and fluorobenzenes, and attempts (11) are also being made to understand these coupling constants on the basis of molecular electronic structure. These spectra are generally complex as the chemical shifts in these molecules are usually of the same order of magnitude as the involved coupling constants. In the present work the high resolution H^1 & F^{19} NMR spectra of the four spin system (ABCX

type) of 1-fluoro, 2,4-dinitrobenzene are obtained and analyzed to determine all the parameters involved. The relative signs of the coupling constants are also determined.

(ii) Experimental:

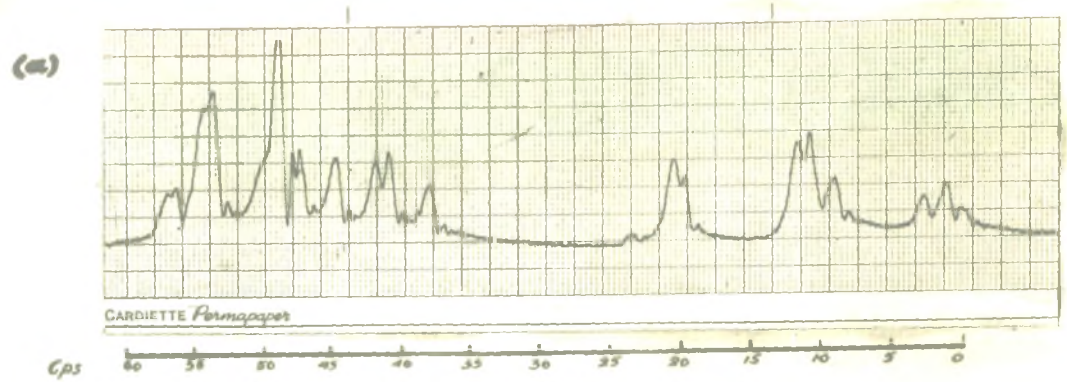
The sample of 1-fluoro, 2,4-dinitrobenzene, obtained from the British Drug House, is used without further purification. The sample is contained in a sealed glass tube of about 5 mm o.d., and about 15cm. long, for both H^1 & F^{19} resonance experiments.

By placing a capillary containing water inside the main sample tube, as an external standard, the chemical shifts of the proton resonance signals of the compound with reference to the signal of water are determined, in the usual manner.

The observed H^1 and F^{19} resonance spectra are shown in Figs. II.1(a) and II.2(a) respectively.

(iii) Theoretical:

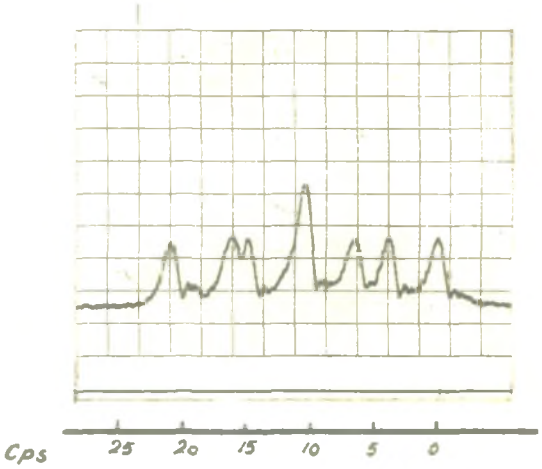
The molecule 1-fluoro, 2,4-dinitrobenzene, is an unsymmetrical four spin system and is of the type ABCX, where all the nuclei are non-equivalent, and all the coupling constants are different from one another. All the zero order eigenfunctions and the corresponding diagonal matrix elements for this system are given in Table II.1.



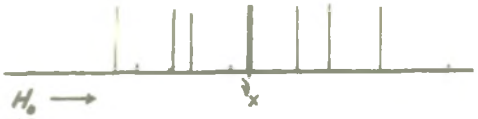
H^1 NMR SPECTRUM OF 1-FLUORO, 2,4- DINITROBENZENE AT 40 Mc/Sec.
(a) EXPERIMENTAL (b) CALCULATED $J_{CH} = 4{\cdot}051$ Cps.

Fig II. 1.

(a)



(b)



F^{19} NMR SPECTRUM OF 1-FLUORO 2,4-DINITROBENZENE AT 40 Mc/Sec.
(a) EXPERIMENTAL (b) CALCULATED
1 Cm = 4·821 Cps

Fig. II. 2

TABLE II.1.

Zero order eigenfunctions and the corresponding diagonal matrix elements for the ABCX system

Sl. No.	F_z	Zero Order eigen-function †	Diagonal Matrix Element $\mathcal{H}_{nn}$
1.	2	$\alpha\alpha\alpha\alpha$	$\frac{1}{2}(\nu_A+\nu_B+\nu_C+\nu_X)+\frac{1}{4}(J_{AB}+J_{BC}+J_{AC}+J_{AX}+J_{BX}+J_{CX})$
2.	1	$\alpha\alpha\alpha\beta$	$\frac{1}{2}(\nu_A+\nu_B+\nu_C-\nu_X)+\frac{1}{4}(J_{AB}+J_{BC}+J_{AC}-J_{AX}-J_{BX}-J_{CX})$
3.	1	$\alpha\alpha\beta\alpha$	$\frac{1}{2}(\nu_A+\nu_B-\nu_C+\nu_X)+\frac{1}{4}(J_{AB}-J_{BC}-J_{AC}+J_{AX}+J_{BX}-J_{CX})$
4.	1	$\alpha\beta\alpha\alpha$	$\frac{1}{2}(\nu_A-\nu_B+\nu_C+\nu_X)+\frac{1}{4}(-J_{AB}-J_{BC}+J_{AC}+J_{AX}-J_{BX}+J_{CX})$
5.	1	$\beta\alpha\alpha\alpha$	$\frac{1}{2}(-\nu_A+\nu_B+\nu_C+\nu_X)+\frac{1}{4}(-J_{AB}+J_{BC}-J_{AC}-J_{AX}+J_{BX}+J_{CX})$
6.	0	$\alpha\alpha\beta\beta$	$\frac{1}{2}(\nu_A+\nu_B-\nu_C-\nu_X)+\frac{1}{4}(J_{AB}-J_{BC}-J_{AC}-J_{AX}-J_{BX}+J_{CX})$
7.	0	$\alpha\beta\alpha\beta$	$\frac{1}{2}(\nu_A-\nu_B+\nu_C-\nu_X)+\frac{1}{4}(-J_{AB}-J_{BC}+J_{AC}-J_{AX}+J_{BX}-J_{CX})$
8.	0	$\beta\alpha\alpha\beta$	$\frac{1}{2}(-\nu_A+\nu_B+\nu_C-\nu_X)+\frac{1}{4}(-J_{AB}+J_{BC}-J_{AC}+J_{AX}-J_{BX}-J_{CX})$

† α denotes the Spin function for $I_z=\frac{1}{2}$ and β for $I_z=-\frac{1}{2}$. The spin functions are written such that, in general, $\alpha\beta\beta\alpha$ would mean $\alpha(A)\,\beta(B)\,\beta(C)\,\alpha(X)$ etc.

The total number of stationary states are actually $2^4=16$ as this is a four spin system. The zero order eigenfunctions and the corresponding diagonal matrix elements for the rest of the eight states are easily obtained by using the following rules{12

Contd.....

If we define an operator σ with the property that when operating on a spin function it transforms "α spins" to "β spins", then

$$\phi^{\circ}_{n+1} = \sigma\left(\phi^{\circ}_{16-n}\right) \qquad (i)$$

If the first and second terms in $\mathcal{H}_{nn}$ are denoted by a_{nn} and b_{nn} such that $\mathcal{H}_{n+1,n+1} = a_{n+1,n+1} + b_{n+1,n+1}$ (ii)

Then $\mathcal{H}_{16-n,16-n}$ is given by

$$\mathcal{H}_{16-n,16-n} = -a_{n+1,n+1} + b_{n+1,n+1} \qquad (iii)$$

TABLE II.2.

Mixed wave functions and energy levels.

State*	Wave Function	Energy
4'	$\cos\theta_+(\alpha\beta\alpha\alpha)+\sin\theta_+(\beta\alpha\alpha\alpha)$	$\frac{1}{2}(\nu_c+\nu_x)+\frac{1}{2}(J_{CX}-J_{AB})+D_+$
5'	$-\sin\theta_+(\alpha\beta\alpha\alpha)+\cos\theta_+(\beta\alpha\alpha\alpha)$	$\frac{1}{2}(\nu_c+\nu_x)+\frac{1}{2}(J_{CX}-J_{AB})-D_+$
7'	$\cos\phi_+(\alpha\beta\alpha\beta)+\sin\phi_+(\beta\alpha\alpha\beta)$	$\frac{1}{2}(\nu_c-\nu_x)-\frac{1}{2}(J_{AB}+J_{CX})+F_+$
8'	$-\sin\phi_+(\alpha\beta\alpha\beta)+\cos\phi_+(\beta\alpha\alpha\beta)$	$\frac{1}{2}(\nu_c-\nu_x)-\frac{1}{2}(J_{AB}+J_{CX})-F_+$
9'	$\cos\phi_-(\alpha\beta\beta\alpha)+\sin\phi_-(\beta\alpha\beta\alpha)$	$-\frac{1}{2}(\nu_c-\nu_x)-\frac{1}{2}(J_{AB}+J_{CX})+F_-$
10'	$-\sin\phi_-(\alpha\beta\beta\alpha)+\cos\phi_-(\beta\alpha\beta\alpha)$	$-\frac{1}{2}(\nu_c-\nu_x)-\frac{1}{2}(J_{AB}+J_{CX})-F_-$
12'	$\cos\theta_-(\alpha\beta\beta\beta)+\sin\theta_-(\beta\alpha\beta\beta)$	$-\frac{1}{2}(\nu_c+\nu_x)+\frac{1}{2}(J_{CX}-J_{AB})+D_-$
13'	$-\sin\theta_-(\alpha\beta\beta\beta)+\cos\theta_-(\beta\alpha\beta\beta)$	$-\frac{1}{2}(\nu_c+\nu_x)+\frac{1}{2}(J_{CX}-J_{AB})-D_-$

* The mixed states are labelled 4', 5' etc. to denote that these wave functions reduce to the basic product functions 4,5 etc. when the chemical shift ($\nu_A-\nu_B$) is large.

The non-vanishing off-diagonal matrix elements are given by the following equations:

$$\left.\begin{aligned} \mathcal{H}_{34} = \mathcal{H}_{67} = \mathcal{H}_{10,11} = \mathcal{H}_{13,14} &= \tfrac{1}{2} J_{BC} \\ \mathcal{H}_{35} = \mathcal{H}_{68} = \mathcal{H}_{9,11} = \mathcal{H}_{12,14} &= \tfrac{1}{2} J_{AC} \\ \mathcal{H}_{45} = \mathcal{H}_{78} = \mathcal{H}_{9,10} = \mathcal{H}_{12,13} &= \tfrac{1}{2} J_{AB} \end{aligned}\right\} \quad \cdots (\text{II}.1)$$

and the rest of these elements are obtained by the condition

$$\mathcal{H}_{mn} = \mathcal{H}_{nm} \qquad \cdots \quad (\text{II}.2)$$

As the states with different values of I_{3x} do not mix, the basic product functions 2 and 15 (Table II.1) will become approximate stationary state wave functions, and the corresponding diagonal matrix elements give the respective eigenvalues. Further, the states 6,7 & 8 do not mix with the states 9,10 & 11. But for a complete solution of the secular equation it is still necessary to solve four 3 x 3 determinents (for the states 3,4 & 5, and 6,7 & 8 and 9,10 & 11, and 12,13 & 14). Explicit expressions for the energy levels in these cases are difficult to derive and a systematic analysis is therefore not usually possible.

But the proton resonance spectrum of the molecule (Fig. II.1(a)) shows two groups of lines separated by about 40 cps. An approximate measurement of the areas under the lines showed that one of the three protons gives rise to the well separated group of lines on the higher field side. If this proton is called C, this may also be treated similar to X,

as a first approximation. Then the basic product functions 3,6,11 & 14 (Table II.1) may also be considered as approximate stationary state wave functions and the diagonal matrix elements give the corresponding eigenvalues. Now, only four 2 x 2 determinants remain to be solved to obtain all the energy levels. The calculations can then be done by a straightforward extension of the method adapted for the ABX systems (2,3).

For convenience of calculation, we define positive quantities D_+, F_+, F_- and D_-, and angles θ_+, ϕ_+, ϕ_- and θ_- satisfying the following relations:

$$D_+ = \tfrac{1}{2}\left[\left\{(\nu_A-\nu_B)+\tfrac{1}{2}\left[(J_{Ac}-J_{Bc})+(J_{Ax}-J_{Bx})\right]\right\}^2 + J_{AB}^2\right]^{1/2}$$

$$F_+ = \tfrac{1}{2}\left[\left\{(\nu_A-\nu_B)+\tfrac{1}{2}\left[(J_{Ac}-J_{Bc})-(J_{Ax}-J_{Bx})\right]\right\}^2 + J_{AB}^2\right]^{1/2}$$

$$F_- = \tfrac{1}{2}\left[\left\{(\nu_A-\nu_B)+\tfrac{1}{2}\left[-(J_{Ac}-J_{Bc})+(J_{Ax}-J_{Bx})\right]\right\}^2 + J_{AB}^2\right]^{1/2}$$

$$D_- = \tfrac{1}{2}\left[\left\{(\nu_A-\nu_B)+\tfrac{1}{2}\left[-(J_{Ac}-J_{Bc})-(J_{Ax}-J_{Bx})\right]\right\}^2 + J_{AB}^2\right]^{1/2} \qquad (II\cdot 3)$$

and

$$\tan 2\theta_+ = \frac{J_{AB}}{(\nu_A-\nu_B)+\tfrac{1}{2}\left[(J_{Ac}-J_{Bc})+(J_{Ax}-J_{Bx})\right]}$$

$$\tan 2\phi_+ = \frac{J_{AB}}{(\nu_A-\nu_B)+\tfrac{1}{2}\left[(J_{Ac}-J_{Bc})-(J_{Ax}-J_{Bx})\right]}$$

$$\tan 2\phi_- = \frac{J_{AB}}{(\nu_A-\nu_B)+\tfrac{1}{2}\left[-(J_{Ac}-J_{Bc})+(J_{Ax}-J_{Bx})\right]} \qquad (II\cdot 4)$$

$$\tan 2\theta_{-} = \frac{J_{AB}}{(\nu_A - \nu_B) + \frac{1}{2}\left[-(J_{AC} - J_{BC}) - (J_{AX} - J_{BX})\right]} \qquad (II.4)$$

In terms of these quantities the mixed wave functions and the corresponding energy levels are obtained in explicit form and are given in Table (II.2).

The different transitions are classified into AB, C and X types and the expressions for the transition frequencies and their relative intensities are given in Tables (II.3), (II.4) and (II.5) respectively for the three types.* In the case of C and X transitions, only those combination lines with non-zero intensities are given.

(iv) Interpretation:

(a) X-Spectrum:- This corresponds to the F^{19} spectrum of the molecule (Fig. II.2(a)). The theoretical spectrum given in Table II.5, shows that there are four strong lines symmetrically disposed about ν_x, and two doublets (Transitions 3 & 4 and 5 & 6) with their centers separated by J_{CX}. The combination lines also form two such doublets, but as they are generally weak they may escape detection.

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* Similar expressions for the transition energies and relative intensities were obtained by Lee and Sutcliffe (13) for the analysis of Spectra of 1:1:2-trifluoro, 1-bromo, 2-chloro ethane. The molecule is described as an ABPX system by these authors.

TABLE II.3.

Transition energies and relative intensities for AB spectrum.

Sl. No.	Transition	Energy w.r.t. $\frac{1}{2}(\nu_A + \nu_B)$	Relative Intensity
1.	$4' \rightarrow 1$	$\frac{1}{2}J_{AB}+\frac{1}{2}(J_{BC}+J_{AC}+J_{AX}+J_{BX})-D_+$	$1+\sin 2\theta_+$
2.	$5' \rightarrow 1$	$\frac{1}{2}J_{AB}+\frac{1}{2}(J_{BC}+J_{AC}+J_{AX}+J_{BX})+D_+$	$1-\sin 2\theta_+$
3.	$11 \rightarrow 4'$	$-\frac{1}{2}J_{AB}+\frac{1}{2}(J_{BC}+J_{AC}+J_{AX}+J_{BX})+D_+$	$1+\sin 2\theta_+$
4.	$11 \rightarrow 5'$	$-\frac{1}{2}J_{AB}+\frac{1}{2}(J_{BC}+J_{AC}+J_{AX}+J_{BX})-D_+$	$1-\sin 2\theta_+$
5.	$7' \rightarrow 2$	$+\frac{1}{2}J_{AB}+\frac{1}{2}(J_{BC}+J_{AC}-J_{AX}-J_{BX})-F_+$	$1+\sin 2\phi_+$
6.	$8' \rightarrow 2$	$\frac{1}{2}J_{AB}+\frac{1}{2}(J_{BC}+J_{AC}-J_{AX}-J_{BX})+F_+$	$1-\sin 2\phi_+$
7.	$14 \rightarrow 7'$	$-\frac{1}{2}J_{AB}+\frac{1}{2}(J_{BC}+J_{AC}-J_{AX}-J_{BX})+F_+$	$1+\sin 2\phi_+$
8.	$14 \rightarrow 8'$	$-\frac{1}{2}J_{AB}+\frac{1}{2}(J_{BC}+J_{AC}-J_{AX}-J_{BX})-F_+$	$1-\sin 2\phi_+$
9.	$9' \rightarrow 3$	$\frac{1}{2}J_{AB}+\frac{1}{2}(J_{AX}+J_{BX}-J_{BC}-J_{AC})-F_-$	$1+\sin 2\phi_-$
10.	$10' \rightarrow 3$	$\frac{1}{2}J_{AB}+\frac{1}{2}(J_{AX}+J_{BX}-J_{BC}-J_{AC})+F_-$	$1-\sin 2\phi_-$
11.	$15 \rightarrow 9'$	$-\frac{1}{2}J_{AB}+\frac{1}{2}(J_{AX}+J_{BX}-J_{BC}-J_{AC})+F_-$	$1+\sin 2\phi_-$
12.	$15 \rightarrow 10'$	$-\frac{1}{2}J_{AB}+\frac{1}{2}(J_{AX}+J_{BX}-J_{BC}-J_{AC})-F_-$	$1-\sin 2\phi_-$
13.	$12' \rightarrow 6$	$\frac{1}{2}J_{AB}-\frac{1}{2}(J_{BC}+J_{AC}+J_{AX}+J_{BX})-D_-$	$1+\sin 2\theta_-$
14.	$13' \rightarrow 6$	$\frac{1}{2}J_{AB}-\frac{1}{2}(J_{BC}+J_{AC}+J_{AX}+J_{BX})+D_-$	$1-\sin 2\theta_-$
15.	$16 \rightarrow 12'$	$-\frac{1}{2}J_{AB}-\frac{1}{2}(J_{BC}+J_{AC}+J_{AX}+J_{BX})+D_-$	$1+\sin 2\theta_-$
16.	$16 \rightarrow 13'$	$-\frac{1}{2}J_{AB}-\frac{1}{2}(J_{BC}+J_{AC}+J_{AX}+J_{BX})-D_-$	$1-\sin 2\theta_-$

TABLE II.4.

Transition energies and relative intensities of C spectrum.

Sl. No.	Transition	Energy w.r.t. ν_C	Relative Intensity
1.	3' → 1	$\frac{1}{2}(J_{AC}+J_{BC}+J_{CX})$	1
2.	9' → 4'	$\frac{1}{2}(J_{CX})+(D_+-F_-)$	$\cos^2(\theta_+-\phi_-)$
3.	10' → 5'	$\frac{1}{2} J_{CX}-(D_+-F_-)$	$\cos^2(\theta_+-\phi_-)$
4.	6' → 2	$\frac{1}{2}(J_{AC}+J_{BC}-J_{CX})$	1
5.	15 → 11	$-\frac{1}{2}(J_{AC}+J_{BC}-J_{CX})$	1
6.	12' → 7'	$-\frac{1}{2} J_{CX}+(F_+-D_-)$	$\cos^2(\phi_+-\theta_-)$
7.	13' → 8'	$-\frac{1}{2} J_{CX}-(F_+-D_-)$	$\cos^2(\phi_+-\theta_-)$
8.	16 → 14	$-\frac{1}{2}(J_{AC}+J_{BC}+J_{CX})$	1
9.			
Combination Lines			
9.	9' → 5'	$\frac{1}{2} J_{CX}-(D_++F_-)$	$\sin^2(\theta_+-\phi_-)$
10.	10' → 4'	$\frac{1}{2} J_{CX}+(D_++F_-)$	$\sin^2(\theta_+-\phi_-)$
11.	12' → 8'	$-\frac{1}{2} J_{CX}-(F_++D_-)$	$\sin^2(\phi_+-\theta_-)$
12.	13' → 7'	$-\frac{1}{2} J_{CX}+(F_++D_-)$	$\sin^2(\phi_+-\theta_-)$

TABLE II.5.

Transition energies and relative intensities of X Spectrum.

Sl. No.	Transition	Energy w.r.t. ν_X	Relative Intensity
1.	2 → 1	$\frac{1}{2}(J_{AX}+J_{BX}+J_{CX})$	1
2.	6 → 3	$\frac{1}{2}(J_{AX}+J_{BX}-J_{CX})$	1
3.	7' → 4'	$\frac{1}{2} J_{CX} +(D_+-F_+)$	$\cos^2(\phi_+-\theta_+)$
4.	8' → 5'	$\frac{1}{2} J_{CX} -(D_+-F_+)$	$\cos^2(\phi_+-\theta_+)$
5.	12' → 9'	$-\frac{1}{2} J_{CX} +(F_--D_-)$	$\cos^2(\phi_--\theta_-)$
6.	13' → 10'	$-\frac{1}{2} J_{CX} -(F_--D_-)$	$\cos^2(\phi_--\theta_-)$
7.	14 → 11	$-\frac{1}{2}(J_{AX}+J_{BX}-J_{CX})$	1
8.	16 → 15	$-\frac{1}{2}(J_{AX}+J_{BX}+J_{CX})$	1
Combination lines			
9.	8' → 4'	$\frac{1}{2} J_{CX}+ (D_++F_+)$	$\sin^2(\theta_+-\phi_+)$
10.	7' → 5'	$\frac{1}{2} J_{CX} -(D_++F_+)$	$\sin^2(\theta_+-\phi_+)$
11.	13' → 9'	$-\frac{1}{2} J_{CX} +(F_-+D_-)$	$\sin^2(\theta_--\phi_-)$
12.	12' → 10'	$-\frac{1}{2} J_{CX} -(F_-+D_-)$	$\sin^2(\theta_--\phi_-)$

The expected strong lines are identified with the lines at 0, 10.34 & 20.73 cps. in the observed spectrum, with the line at 10.34 cps. being assumed as a superposition of two strong lines. The two doublets are identified with the lines at 3.91 & 6.47 cpss. and 14.79 & 16.03 cps. But an unambiguous assignment of the lines to the transitions cannot be made unless the signs of the coupling constants $\bar{J}_{CX}$ and $(J_{AX} + J_{BX})$ are known. By assuming the different possible combinations of signs for these constants, the following values are obtained.

$$|J_{CX}| = |\bar{J}_{AX} + J_{BX}| = 10.4 \pm 0.2 \text{ cps} \qquad (II.5)$$

And

$$2|D_+ - F_+| = 1.2 \pm 0.2 \text{ cps or } 2.6 \pm 0.2 \text{ cps}$$

$$\& \quad 2|D_- - F_-| = 2.6 \pm 0.2 \text{ cps or } 1.2 \pm 0.2 \text{ cps} \qquad (II.6)$$

according as J_{CX} is positive or negative respectively.

The weak line at 19.11 cps. is then one of the four combination lines, and its final assignment is made later.

By comparing the value of J_{CX} obtained here, with the H-F coupli ng constants observed by earlier workers (2,5), the proton which is ortho to fluorine is identified with C. Then J_{AX} and J_{BX} are the meta H-F coupling constants.

(b) C Spectrum:- The theoretical spectrum of C, given in Table II.4, can be subdivided for convenience of identification in a manner exactly similar to the case of the X spectrum. But the combination lines in this case may be considerably stronger than in the case of X as the chemical shift of C with respect to AB is not very large.

The expected strong lines are identified with the lines at 1.07, 10.77, 11.68 and 20.59 cps. of the observed spectrum (Fig. II.1(a)), but again proper assignment depends on the signs of coupling constants J_{CX} and $J_{BC} + J_{AC}$, so that as in the case of the X spectrum, only the magnitudes of these are determined. They are

$$|J_{CX}| = 10.2 \pm 0.2 \text{ cps} \qquad |J_{BC} + J_{AC}| = 9.3 \pm 0.2 \text{ cps} \qquad \text{-(II.7)}$$

The value of J_{CX} obtained here agrees well with that in Eq.(II.5), thus providing a check on the assignment.

The doublets in the C spectrum are checked after the AB spectrum has been analysed.

(c) AB Spectrum:- The theoretical AB spectrum, given in Table II.3, consists of four quartets which may be called the D_+ quartet, F_+ quartet, F_- quartet and D_- quartet respectively. The frequency and intensity distributions in every one of these quartets are just similar to the quartets in the ABX type of spectra (2,3). The frequencies of the quartet

centers, for the D_+, F_+, F_- and D_- quartets, with reference to $\frac{1}{2}(\nu_A+\nu_B)$ are given respectively by

$$\left.\begin{aligned}
&\tfrac{1}{4}\left[(J_{Bc}+J_{Ac})+(J_{Ax}+J_{Bx})\right]\\
&\tfrac{1}{4}\left[(J_{Bc}+J_{Ac})-(J_{Ax}+J_{Bx})\right]\\
&\tfrac{1}{4}\left[-(J_{Bc}+J_{Ac})+(J_{Ax}+J_{Bx})\right]\\
&\tfrac{1}{4}\left[-(J_{Bc}+J_{Ac})-(J_{Ax}+J_{Bx})\right]
\end{aligned}\right\} \quad \ldots(II.8)$$

Each one of the quartets consists of a pair of doublets whose separation is J_{AB}, and the separation between alternate lines in a quartet is $2D_+$ or $2F_+$ etc., according as it is a D_+ quartet or F_+ quartet etc.

As the frequencies of AB spectrum remain unchanged if J_{AB} is replaced by $-J_{AB}$, only $|J_{AB}|$ can be found from the analysis.

From the observed frequencies, by trial and error, three quartets are first picked up with centers at 44.2, 49.3 and 53.7 cps. The separations between alternate lines in these quartets are 9.1, 11.6 and 4.3 cps., respectively. From these three quartets it is found that

$$|J_{AB}| = 2.9 \pm 0.2 \text{ cps} \qquad \ldots (II.9)$$

For the fourth quartet it is necessary to assume that the two central lines coincide, within experimental error, to form a single strong line, and this was identified with the line at 49.05 cps., in the spectrum. Now, from the expressions for the intensities, it will be seen that in this case the

two outer lines of the quartet would have zero intensity, i.e. the quartet reduces to a single intense line. This is supported by the fact that no lines are observed separated by 2.9 cps., on either side, from the line at 49.05 cps.

(d) Signs of the coupling constants:- The four quartets in the AB spectrum may be assigned as D_+ quartet, F_+ quartet etc. depending on the frequencies of their centers. But this, in turn, depends on the signs of $(J_{BC}+J_{AC})$ and $(J_{AX}+J_{BX})$ which are not known. If ν_a, ν_b, ν_c and ν_d are the frequencies of the four quartet centers such that $\nu_a < \nu_b < \nu_c < \nu_d$, by assuming different combinations of signs of $(J_{BC}+J_{AC})$ and $(J_{AX}+J_{BX})$ four different assignments are possible as given in Table II.6.

By comparing the values of $|D_+ - F_+|$ and $|D_- - F_-|$ for all the four assignments with those obtained in the analysis of X spectrum, the corresponding sign of J_{CX} is inferred in each case. This is given in the last column of Table II.6.

The correct assignment among these four may be found by calculating the frequencies of the doublets in C spectrum, and the weak combination line in X spectrum, and comparing with the observed frequencies. This calculation indicated that only assignments 1 and 4 would give satisfactory agreement, thus ruling out assignments 2 and 3 in Table II.6. Thus it is concluded that $(J_{BC}+J_{AC})$, $(J_{AX}+J_{BX})$ and J_{CX} are all of the same sign.

TABLE II.6.

ASSIGNMENT OF QUARTETS IN AB SPECTRUM.

Srl. No.	Sign of $(J_{BC}+J_{AC})$	Sign of $(J_{AX}+J_{BX})$	Assignment of Quartets				Inferred * sign of J_{CX}
			ν_a	ν_b	ν_c	ν_d	
1.	+	+	D_-	F_+	F_-	D_+	+
2.	-	+	F_-	D_+	D_-	F_+	+
3.	+	-	F_+	D_-	D_+	F_-	-
4.	-	-	D_+	F_-	F_+	D_-	-

* See text.

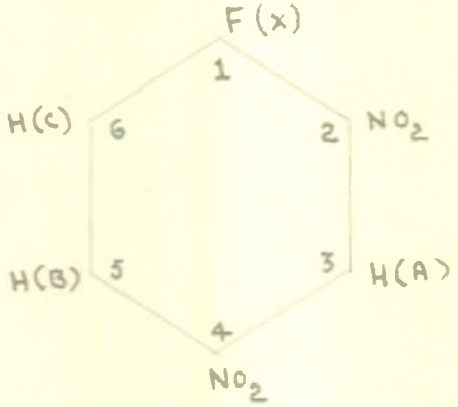

Fig II.3

These two assignments (1 & 4) give the same frequencies and intensities for AB, C & X spectra.

(v) Results:

The values of $(\nu_A - \nu_B)$, $(J_{BC} - J_{AC})$ and $(J_{AX} - J_{BX})$ obtained for assignment 1* (Table II.6) by first calculating $D_+ \cos 2\theta_+$, $F_+ \cos 2\phi_+$†, $F_- \cos 2\phi_-$ and $D_- \cos 2\theta_-$ are

$$\left.\begin{aligned} \nu_A - \nu_B &= 5.9 \text{ cps} \\ J_{BC} - J_{AC} &= 8.0 \text{ cps} \\ J_{AX} - J_{BX} &= 2.7 \text{ cps} \end{aligned}\right\} \quad \ldots (II.10)$$

The factors $D_+ \cos 2\theta_+$ etc. can also be negative, but this only interchanges the roles of A and B in the above values.

All the parameters obtained from this analysis may then be summarized as

$$\left.\begin{aligned} &\nu_A - \nu_c = 41.2 \text{ cps} \qquad \nu_B - \nu_c = 35.3 \text{ cps}. \\ &|J_{AB}| = 2.9 \text{ cps}. \quad J_{BC} = 8.7 \text{ cps}. \quad J_{AC} = 0.6 \text{ cps}. \\ &J_{AX} = 6.5 \text{ cps}. \quad J_{BX} = 3.8 \text{ cps}. \quad J_{CX} = 10.4 \text{ cps} \end{aligned}\right\} \quad (II.11)$$

---

* Calculation on the basis of assignment 4, only reverses the signs of the coupling constants J_{BC}, J_{AC}, J_{AX} and J_{BX}.

† $F_+ \cos 2\phi_+$ becomes zero as $2F_+ = J_{AB}$ according to this assignment. But this is not used in the calculation as $F_+ \cos 2\phi_+$ is highly sensitive to small errors in F_+. This difficulty is removed by perturbation calculations (see sec. vi)

(vi) Perturbation Calculations:

An attempt has now been made to refine the analysis by perturbation calculations. The procedure followed for these calculations is similar to that used by Fessenden and Waugh (14) in the analysis of the spectrum of trans-propenyl benzene. Consider, for example, the factor of the secular equation for obtaining the energy levels 3,4 and 5.

$$\begin{vmatrix} \mathcal{H}_{33} & \mathcal{H}_{34} & \mathcal{H}_{35} \\ \mathcal{H}_{43} & \mathcal{H}_{44} & \mathcal{H}_{45} \\ \mathcal{H}_{53} & \mathcal{H}_{54} & \mathcal{H}_{55} \end{vmatrix} = 0 \quad \ldots \quad (\text{II}.12)$$

We have earlier set $\mathcal{H}_{34} = \mathcal{H}_{43} = \frac{1}{2}J_{BC} = 0$, and $\mathcal{H}_{35} = \mathcal{H}_{53} = \frac{1}{2}J_{AC} = 0$, as a first approximation and diagonalized the matrix i.e., the lower quadratic block of the determinant is solved. The resulting energy levels are

$$\left.\begin{aligned} E_3^{(0)} &= \mathcal{H}_{33} = \tfrac{1}{2}(\nu_A+\nu_B-\nu_C+\nu_X) + \tfrac{1}{4}(J_{AB}-J_{BC}-J_{AC}+J_{AX}+J_{BX}-J_{CX}) \\ E_4^{(0)} &= \tfrac{1}{2}(\nu_C+\nu_X) + \tfrac{1}{4}(J_{CX}-J_{AB}) + D \\ E_5^{(0)} &= \tfrac{1}{2}(\nu_C+\nu_X) + \tfrac{1}{4}(J_{CX}-J_{AB}) - D \end{aligned}\right\} \ldots (\text{II}.13)$$

((0) denotes the values without application of the perturbation).

The corresponding wave functions are given by

$$\left.\begin{aligned}\phi_3^{(0)} &= \alpha\alpha\beta\alpha \\ \phi_4^{(0)} &= \cos\theta_+(\alpha\beta\alpha\alpha) + \sin\theta_+(\beta\alpha\alpha\alpha) \\ \phi_5^{(0)} &= -\sin\theta_+(\alpha\beta\alpha\alpha) + \cos\theta_+(\beta\alpha\alpha\alpha)\end{aligned}\right\} \quad \ldots (\text{II}.14)$$

Now $\phi_3^{(0)}$, $\phi_4^{(0)}$ and $\phi_5^{(0)}$ are eigenfunctions of the Hamiltonian

$$\mathcal{H}^{(0)} = \sum_i \gamma_i I_{zi} + J_{AB}\vec{I}_A\vec{I}_B + J_{Ax}\vec{I}_A.\vec{I}_x + J_{Bx}\vec{I}_B.\vec{I}_x$$

$$+ J_{cx}\vec{I}_c.\vec{I}_x + J_{Bc}I_{zB}I_{zc} + J_{Ac}I_{zA}I_{zc} \quad \ldots (\text{II}.15)$$

The remaining part of the total Hamiltonian (as in Eqns. (I.1), (I.2) & (I.3)) can now be treated as a perturbation. If this is called $\mathcal{H}^{(1)}$ then

$$\mathcal{H}^{(1)} = J_{Bc}(I_{xB}I_{xc} + I_{yB}I_{yc}) + J_{Ac}(I_{xA}I_{xc} + I_{yA}I_{yc}) \quad \ldots (\text{II}.16)$$

$\mathcal{H}^{(1)}$ will not have any diagonal elements i.e., the first order perturbation energies are zero. This is because J_{BC} and J_{AC} have already been taken into account to the extent they affect the diagonal matrix elements in the secular equation. This is clear from Eqns. (II.15) and (II.16).

The off-diagonal elements of $\mathcal{H}^{(1)}$ are given by the following relations:

$$\left.\begin{aligned}\mathcal{H}_{34}^{(1)} = \mathcal{H}_{43}^{(1)} &= (\phi_3^{(0)}|\mathcal{H}^{(1)}|\phi_4^{(0)}) = \cos\theta_+\mathcal{H}_{34} + \sin\theta_+\mathcal{H}_{35} \\ &= \cos\theta_+(\tfrac{1}{2}J_{Bc}) + \sin\theta_+(\tfrac{1}{2}J_{Ac}) \\ \text{Similarly } \mathcal{H}_{35}^{(1)} = \mathcal{H}_{53}^{(1)} &= -\sin\theta_+(\tfrac{1}{2}J_{Bc}) + \cos\theta_+(\tfrac{1}{2}J_{Ac}) \\ \text{and } \mathcal{H}_{45}^{(1)} = \mathcal{H}_{54}^{(1)} &= 0\end{aligned}\right\} \quad \ldots (\text{II}.17)$$

Now the energies are calculated by the second order perturbation formula

$$E_n = \mathcal{H}_{nn}^{(0)} + \sum_{kn}{}' \frac{\left[\mathcal{H}_{nk}^{(1)}\right]^2}{\mathcal{H}_{nn}^{(0)} - \mathcal{H}_{kk}^{(0)}} \qquad \ldots \quad (II..8)$$

$\sum_{kn}{}'$ denotes summation over all values of k except k = n.
The corresponding wave functions are obtained by the formula

$$\phi_n = \phi_n^{(0)} + \sum_{mn}{}' \frac{\mathcal{H}_{mn}^{(1)}}{E_n^{(0)} - E_m^{(0)}} \phi_m^{(0)}$$

$$+ \sum_{kn}{}' \left[\sum_{mn}{}' \frac{\mathcal{H}_{km}^{(1)} \mathcal{H}_{mn}^{(1)}}{\left(E_n^{(0)} - E_k^{(0)}\right)\left(E_n^{(0)} - E_m^{(0)}\right)} - \frac{\mathcal{H}_{nn}^{(1)} \mathcal{H}_{kn}^{(1)}}{\left(E_n^{(0)} - E_k^{(0)}\right)^2} \right] \phi_k^{(0)}$$

...(II.19)

Now, using the values of the parameters in Eq.(II.11) and with the help of the procedure described by the equations (II.12) to (II.17), the corrections to the different energy levels $\Delta E_n = E_n - \mathcal{H}_{nn}^{(0)}$ have been obtained by Eq. (II.18). This correction is not more than 0.6 cps. in any case, and is not even that much for many energy levels. This justifies the approximation that has been used, in Sec. (iii) to calculate the energy levels.

The corrections for the transition energies are then calculated, and the analysis, carried out taking these corrections into account, yields a new set of parameters slightly different from those in Eq. (II.11). The perturbation calculations and analysis are repeated once again with

this new set of parameters, and after this the corrections to the energy levels are found to be practically constant. The set of parameters finally obtained may be summarised as

$\nu_A - \nu_{H_2O} = 137.0 \pm 0.5$ cps.*
$\nu_B - \nu_C = 34.1 \pm 0.3$ cps.
$\nu_A - \nu_C = 40.6 \pm 0.3$ cps.
$\nu_A - \nu_B = 6.5 \pm 0.3$ cps.

$J_{BC} = J_0^{HH} = 8.65 \pm 0.3$cps.
$|J_{AB}| = J_m^{HH} = 2.85 \pm 0.2$cps.
$J_{AC} = J_p^{HH} = 0.65 \pm 0.3$cps.
$J_{CX} = J_0^{HF} = 10.35 \pm 0.2$cps.
$J_{AX} = J_m^{HF} = 6.45 \pm 0.3$cps.
$J_{BX} = J_m^{HF} = 3.85 \pm 0.3$cps.

.. (II.20

Using these parameters, the exact wave functions are calculated using Eq. (II.19). These wave functions along with the corrections to the corresponding energy levels are given in Table II.7.

The transition frequencies and their relative intensities calculated on the basis of Eq. (II.20) for the AB, C and X spectra are given in Tables (II.8), II.9 and II.10 respectively along with the corresponding observed frequencies. The calculated H^1 and F^{19} spectra are shown in Figs. II.1(b) and II.2(b) respectively.** The agreement between observed and calculated spectra is fairly satisfactory.

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* The bulk diamagnetic susceptibility correction is not applied.

** The line heights in Figs. II.1(b) & II.2(b) are drawn roughly proportional to the calculated relative intensities. It may be noted that in the observed spectrum the intensities are given by the areas under the lines.

TABLE II.7.

Exact eigenfunctions obtained after perturbation calculations and the corrections to the corresponding energy levels.

State*	Wave function ϕ_n †	Correction to the energy level ΔE_n
3'	$\phi_3^0 + 0.12\,\phi_4^0 + 0.015\,\phi_5^0$	0.58
4'	$-0.135\,\phi_3^0 + 0.94\,\phi_4^0 + 0.355\,\phi_5^0$	-0.55
5'	$0.025\,\phi_3^0 - 0.335\,\phi_4^0 + 0.945\,\phi_5^0$	-0.03
6'	$\phi_6^0 + 0.115\,\phi_7^0 + 0.01\,\phi_8^0$	0.49
7'	$0.10\,\phi_6^0 + 0.825\,\phi_7^0 + 0.565\,\phi_8^0$	-0.38
8'	$0.055\,\phi_6^0 - 0.615\,\phi_7^0 + 0.79\,\phi_8^0$	-0.11
9'	$0.99\,\phi_9^0 + 0.125\,\phi_{10}^0 + 0.02\,\phi_{11}^0$	0.02
10'	$-0.13\,\phi_9^0 + 0.99\,\phi_{10}^0 + 0.14\,\phi_{11}^0$	0.59
11'	$-0.005\,\phi_9^0 - 0.145\,\phi_{10}^0 + \phi_{11}^0$	-0.61
12'	$0.985\,\phi_{12}^0 + 0.16\,\phi_{13}^0 + 0.02\,\phi_{14}^0$	0.02
13'	$-0.165\,\phi_{12}^0 + 0.985\,\phi_{13}^0 + 0.115\,\phi_{14}^0$	0.48
14'	$-0.005\,\phi_{12}^0 - 0.12\,\phi_{13}^0 + \phi_{14}^0$	-0.50

* Nos. as in Table II.1.

† ϕ_n^0 are the zero order eigen-functions, as in Table II.1.

TABLE II.8.

Calculated transition frequencies and relative intensities, and observed frequencies for the AB spectrum.

Transition No. †	Calculated frequency* (in c.p.s.)	Observed # frequency (in c.p.s.)	Calculated Relative Intensity
2	57.43	57.22	0.40
10	56.48	56.51	0.77
3	54.51	54.51	1.56
11	53.66	53.75	1.30
1	53.20		1.32
6	51.57	—	0.05
4	50.38	50.17	0.22
14	50.07		0.69
5	48.72	49.05	1.66
7	48.72		1.77
15	47.24	47.46	1.37
8	45.87	—	0.01
9	44.86	44.96	1.54
12	42.04	42.04	1.01
13	40.91	41.16	1.60
16	38.08	38.15	0.88

† Nos. as in Table II.3.

* With $\frac{1}{2}(\nu_A+\nu_B)$= 48.72cps.

Standard deviations vary between 0.05 and 0.18cps.

TABLE II.9.

Calculated transition frequencies and relative intensities, and observed frequencies for the C spectrum.

Transition No. †	Calculated frequency* (in cps.)	Observed # frequency (in cps.)	Calculated Relative Intensity
10	23.92	23.59	0.08
1	20.64	20.57	1.29
3	19.69	19.73	1.18
2	12.33		0.73
12	11.74	11.68,	0.25
5	11.34	10.77	0.73
4	10.37		1.27
7	8.87	9.07	0.89
9	8.06	—	0.03
6	2.58	2.52	0.67
8	1.08	1.07	0.77
11	-0.29	0.00	0.17

† Nos. as in Table II.4

* with ν_c = 11.40cps.

Standard deviations vary from 0.05 to 0.18cps.

TABLE II.10.

Calculated transition frequencies and relative intensities, and observed frequencies for the X spectrum.

Transition No.†	Calculated frequency* (in cps.)	Observed frequency# (in cps.)	Calculated Relative Intensity
1	20.64	20.73	1.00
9	19.00	19.11	0.10
11	16.50	—	0.001
3	16.13	16.03	0.96
4	14.77	14.79	0.91
10	11.90	—	0.06
2	10.37	10.34	1.03
5	10.26		1.03
6	6.43	6.47	1.00
7	3.96	3.91	1.03
8	0.00	0.00	1.00
12	-5.20	—	0.001

† Nos. as in Table II.5.

* With ν_x = 10.32cps.

Standard deviations vary between 0.07 and 0.14cps.

(vii) Discussion:-

The values of the different coupling constants obtained here compare favourably with those obtained by earlier workers (1-10). But the two meta H-F coupling constants (J_{AX} and J_{BX}) obtained here differ considerably from one another.

It has been found definitely, from the analysis that the ortho and meta H-F coupling constants are of the same sign as the ortho and para H-H coupling constants. This supports the observation of Bak, Shoolery and Williams (5) in the case of deuterated fluorobenzenes.

As J_{AC} represents the para H-H coupling constant when $(\nu_A - \nu_B)$ is positive, we find that the proton para to C (i.e. at the position 3) is least shielded of the three protons in the molecule. Thus the three protons are identified from the analysis. That the A,B & C protons, as given in Fig. II.3 are shielded in the increasing order of magnitude is in conformity with the results obtained on the chemical shifts of ortho, meta and para protons in monosubstituted benzenes by Corio and Dailey (15).

REFERENCES.

1. Baker. E. B., J. Chem. Phys. 23, 984, (1955).

2. Gutowsky. H. S., Holm. C. H., Saika. A. and Williams.G.A. J. Am. Chem. Soc. 79, 4596 (1957).

3. Bernstein. H. J., Pople. J. A. and Schneider. W. G., Can. J. Chem. 35, 65, (1957).

4. Pople. J. A., Schneider. W. G. and Bernstein. H. J., Can. J. Chem. 35, 1060, (1957).

5. Schneider. W. G., Bernstein. H. J. and Pople. J. A., Can. J. Chem. 35, 1487, (1957).

6. Bak. B., Shoolery. J. N., and Williams. G. A., J. Mol. Spectroscopy. 2, 525, (1958).

7. Richards. R. E. and Schaeffer. T. P., Trans. Farad. Soc. 54, 1280, (1958); 54, 1447, (1958).

8. Richards. R. E. and Schaeffer. T. P., Proc. Roy. Soc. (London), 246A, 429 (1958).

9. Leane. J. B. and Richards. R. E., Trans. Farad. Soc. 55, 707, (1959).

10. Fessenden. R. W. and Waugh. J. S., J. Chem. Phys. 31, 996, (1959).

11. Williams. G. A. and Gutowsky. H. S., J. Chem. Phys. 30, 717, (1959).

12. Corio. P. L., J. Chem. Phys. 29, 682, (1959).

13. Leane. J. and Sutcliffe. L. H., Trans. Farad. Soc. 54, 308, (1958).

14. Fessenden. R. W. and Waugh. J. S., J. Chem. Phys. 30, 944, (1959).

15. Corio. P. L. and Dailey. B.P., J. Am. Chem. Soc. 78, 3043, (1956).

CHAPTER III.

PROTON RESONANCE SPECTRA OF SOME PARA DISUBSTITUTED BENZENES

PROTON RESONANCE SPECTRA OF SOME PARA-DISUBSTITUTED BENZENES.

A B S T R A C T.

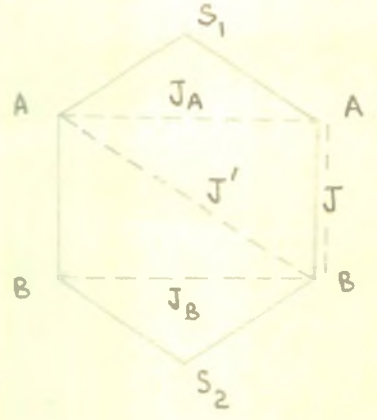
The spectra of a number of p-disubstituted benzenes were analyzed earlier by Richards & Schaeffer by assuming that the two meta H-H coupling constants are equal and that the para H-H coupling constant is zero. In the present work a method for analysing this type of spectra, to obtain all the parameters, without making any simplifying assumptions, is proposed. The proton resonance spectra of P-bromochlorobenzene, p-Chlorotoluene and p-Chloroiodobenzene are obtained and analyzed as examples and all the parameters are determined in each case. The general form of this type of spectra for different values of chemical shift is discussed.

(i) Introduction:

The general theory of the spectra of four spin systems, which can be divided into two pairs of two equivalent nuclei (A_2 B_2 type) has been discussed by Pople, Schneider & Bernstein (1,2). They showed that the total number of transitions in the spectrum are 28, out of which there are four combination transitions, and among the remaining transitions 12 arise due to the two 'A' nuclei and the other 12 due to the two 'B' nuclei. These 24 transitions have their frequencies symmetrically disposed about the center of the spectrum $\frac{1}{2}(\nu_A+\nu_B)$, and the 'A' transitions form a mirror image of the 'B' transitions with respect to this center. Explicit expressions, in terms of the involved parameters, can be

derived for only 6 of the 12 'A' (or B) transitions, as it is necessary to solve a 4 x 4 determinent to obtain the expressions for four of the energy levels involved in the remaining six transitions. A straight forward analysis cannot therefore be carried out, and the spectrum depends on the chemical shift and the spin coupling constants in a rather complicated manner. Pople et.al (1,2), however, proposed some practical methods of analysis for some special cases of this type of spectra (a) when the two AB coupling constants are equal and (b) when one pair of nuclei are more strongly coupled than the other.

The spectra of p-disubstituted benzenes (where the substituents do not interfere in the spectrum) belong to a different case of A_2B_2 spectra, as the nuclei in each pair are strongly coupled to nearly the same extent. Richards and Schaeffer (3) (hereafter referred to as RS) have recently studied the proton resonance spectra of a number of these compounds at 29.92 Mc/Sec. They have made the simplifying assumptions, in all the cases, that $J_A = J_B$, and $J' = 0$ (Fig. III.1) and carried out the analysis. As



(S_1 and S_2 are substituents)

Fig III.1

shown later in this chapter there is no pressing necessity, however, to make these assumptions for analyzing these spectra.

We have here studied again three p-disubstituted benzenes at 40 Mc/Sec. An exact analysis is done without making any special assumptions, and all the parameters are obtained. A general method of analyzing spectra of this type is proposed.

(ii) Experimental:

The molecules studied here are p-bromochlorobenzene, p-chlorotoluene and p-chloroiodobenzene. All the compounds are obtained from British Drug House, and are used without further purification. p-Chlorotoluene is a liquid, and the other two compounds are solids. For p-chloroiodobenzene a solution in ethanol, and for p-bromochlorobenzene a solution in ether are used for the experiment*. The absolute chemical shifts are determined earlier by RS and are not determind again in the present work. The experimental spectra of p-bromochlorobenzene, p-chlorotoluene, & p-chloroiodobenzene are shown in Figs. III.2(a), III.3(a) and III.4(a) respectively.

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* These solvents are the same as those used by RS for these compounds.

The observed line positions are all expressed with respect to the center of the spectrum, in each case, to facilitate comparison with the theoretical spectrum.

(iii) Method of Analysis:

There are five parameters to be obtained from the analysis out of which one is the chemical shift between the two equivalent sets of nuclei, and four are spin coupling constants (See Fig. III.1).

The complete spin matrix for the A_2B_2 type of molecule, and the explicit expressions, for the energy levels and the corresponding wave functions, and transition energies and their relative intensities, in cases where these can be derived, are given by Pople, et.al (1,2). The notation employed by them is freely used throughout this chapter without specification. The calculation can be conveniently done in terms of new quantities K,L,M & N defined as below:

$$\left.\begin{aligned} K &= J_A + J_B & N &= J + J' \\ M &= J_A - J_B & L &= J - J' \end{aligned}\right\} \qquad \text{(III.1).}$$

Explicit expressions for the energy levels are easily obtained for all but four levels which were labelled as $1s_0'$, $2s_0'$, $3s_0'$ & $4s_0'$. It is necessary to solve a 4 x 4 determinent for this and if we denote the energy values corresponding to these four states as E_1, E_2, E_3 and E_4

respectively, these are given by the roots of the fourth power equation,

$$(K+E)\left[E^3+NE^2-\Xi\left\{\frac{1}{4}N^2+(\gamma_0\delta)^2\right\}-\frac{1}{4}N^3\right]-$$

$$\frac{1}{4}L^2\left[3E^2-\left\{\frac{3}{4}N^2+(\gamma_0\delta)^2\right\}\right]=0 \quad \ldots (\text{III}.2)$$

The exact wave functions for these four levels can be expressed as in Eq. (I.5). If E_1, E_2, E_3 and E_4 are known these wave functions can be calculated with the help of Eqns. (I.5), (I.6) and (I.7).

Six of the twelve 'A' (or B) transitions involve these energy levels and the energies of these transitions may be expressed in terms of E_1, E_2, E_3 and E_4. The transition energies of all the 12 'A' (or B) transitions and their relative intensities, are given in Table III.1.

To proceed with the analysis, taking a typical half of the spectrum, the lines 1 and 3 (line Nos. as in Table III.1). may first be identified The identification is easier if an approximate value of N is known, as the separation between the lines is N. (In the case of p-disubstituted benzenes N is equal to the sum of the ortho and para H-H coupling constants, and may be expected to be nearly about 9.0 cps. from the known data on these constants in other compounds. It is reasonable to expect like this as the coupling constants are not, in general, found to be much sensitive to substitution). If these lines

TABLE III.1 †

Transition Energies and relative intensities of 'A' Spectrum

Serial No.	Transition.	Energy w.r.t. $\frac{1}{2}(\nu_A+\nu_B)$	Relative intensity ††
1.	$1S_1' \rightarrow S_2$	$\frac{1}{2}N+\frac{1}{2}\left[(\nu_0\delta)^2+N^2\right]^{\frac{1}{2}}$	$1-\sin 2\phi$
2.	$1S_0' \rightarrow 1S_1'$	$-\frac{1}{2}\left[N^2+(\nu_0\delta)^2\right]^{\frac{1}{2}}-E_1$	$\left[\cos\phi\,(a_{11}+a_{14})+\sin\phi\,(a_{12}+a_{14})\right]^2$
3.	$S_{-2} \rightarrow 1S_{-1}'$	$-\frac{1}{2}N+\frac{1}{2}\left[(\nu_0\delta)^2+N^2\right]^{\frac{1}{2}}$	$1+\sin 2\phi$
4.	$1S_{-1}' \rightarrow 2S_0'$	$E_2-\frac{1}{2}\left[(\nu_0\delta)^2+N^2\right]^{\frac{1}{2}}$	$\left[\cos\phi\,(a_{22}+a_{24})+\sin\phi\,(a_{21}+a_{24})\right]^2$
5.	$3S_0' \rightarrow 2S_1'$	$\frac{1}{2}\left[(\nu_0\delta)^2+N^2\right]^{\frac{1}{2}}-E_3$	$\left[\cos\phi\,(a_{32}+a_{34})+\sin\phi\,(a_{31}+a_{34})\right]^2$
6.	$2S_{-1}' \rightarrow 4S_0'$	$E_4+\frac{1}{2}\left[(\nu_0\delta)^2+N^2\right]^{\frac{1}{2}}$	$\left[\cos\phi\,(a_{41}+a_{44})-\sin\phi\,(a_{42}+a_{44})\right]^2$
7.	$4S_0' \rightarrow 2S_1'$	$\frac{1}{2}\left[(\nu_0\delta)^2+N^2\right]^{\frac{1}{2}}-E_4$	$\left[\cos\phi\,(a_{42}+a_{44})+\sin\phi\,(a_{41}+a_{44})\right]^2$
8.	$2S_{-1}' \rightarrow 3S_0'$	$E_3+\frac{1}{2}\left[(\nu_0\delta)^2+N^2\right]^{\frac{1}{2}}$	$\left[\cos\phi\,(a_{31}+a_{34})-\sin\phi\,(a_{32}+a_{34})\right]^2$
9.	$2a_0' \rightarrow 2a_1'$	$\frac{1}{2}\left[(\nu_0\delta+N)^2+L^2\right]^{\frac{1}{2}}+\frac{1}{2}(N^2+L^2)^{\frac{1}{2}}$	$\sin^2(\theta_a-\psi_+)$
10.	$2a_{-1}' \rightarrow 1a_0'$	$\frac{1}{2}\left[(\nu_0\delta-N)^2+L^2\right]^{\frac{1}{2}}+\frac{1}{2}(N^2+L^2)^{\frac{1}{2}}$	$\cos^2(\theta_a+\psi_-)$
11.	$1a_0' \rightarrow 2a_1'$	$\frac{1}{2}\left[(\nu_0\delta+N)^2+L^2\right]^{\frac{1}{2}}-\frac{1}{2}(N^2+L^2)^{\frac{1}{2}}$	$\cos^2(\theta_a-\psi_+)$
12.	$2a_{-1}' \rightarrow 2a_0'$	$\frac{1}{2}\left[(\nu_0\delta-N)^2+L^2\right]^{\frac{1}{2}}-\frac{1}{2}(N^2+L^2)^{\frac{1}{2}}$	$\sin^2(\theta_a+\psi_-)$

† The expressions for transitions 1, 3, 9, 10, 11 & 12 are the same as those on P. 144 of ref. (2)

†† a_{11} etc. are the coefficients when the wave functions corresponding $1S_0'$, $2S_0'$, $3S_0'$ and $4S_0'$ are expressed as in Eqn. (P. 5).

are fixed, at least tentatively, $\nu_0\delta$ and N are easily obtained.

In molecules like the p-disubstituted benzenes one might expect the value of M to be usually small, and N and L may be nearly equal. Then the lines 9 and 10 will lie close to 1 and lines 11 and 12 will lie close to 3. Sometimes, these lines (9 to 12) may not be separated sufficiently from lines 1 and 3, to be observed. These transitions may therefore be considered at the end of the analysis.

We will now be left with the six transitions 2,4,5,6,7 & 8 and these are determined by the roots of the Eq. (III.2), in which two quantities K and L^2 are yet to be determined ($\nu_0\delta$ and N are already known from the identification of lines 1 and 3). From Table III.1 it can be seen that the sum of the transition frequencies of 5 and 8 as well as that of 6 and 7 are both equal to $\left[(\nu_0\delta)^2+N^2\right]^{1/2}$. The value of this factor is known, and therefore we can pick up from the rest of the lines in the observed spectrum two pairs of lines such that the sum of the frequencies of the lines with respect to $\frac{1}{2}(\nu_A+\nu_B)$ in each pair is equal to $\left[(\nu_0\delta)^2+N^2\right]^{1/2}$. If the frequencies of these lines are, say ν_5 & ν_8 and ν_6 & ν_7 we find that

$$E_3 = \pm \frac{\nu_5 - \nu_8}{2} \quad \text{and} \quad E_4 = \pm \frac{\nu_6 - \nu_7}{2} \qquad \ldots (III.3)$$

From this identification we therefore get two probable values for E_3 and two for E_4, out of which, one is to be discarded in each case. If we substitute these four roots of E in Eqn. (III.2) we get four equations each involving K and L^2.

As mentioned earlier, we know that the values of L and N are near to each other, as the para H-H coupling constant is expected to be small. So, tentatively putting L = N (N being known already) K might be determined from every one of the four equations obtained above. Now the roots of E, which yield the values of K that are positive and close to each other and also lying in the range estimated from the known meta H-H coupling constants, are chosen as the proper roots E_3 and E_4. The corresponding two equations involving K & L^2 can then be solved to obtain K and L.

The other roots E_1 and E_2 can be easily determined and if the lines 2 and 4, involving these energy levels, are satisfactorily accounted for, in the observed spectrum, a check on the above identification of lines 5,6,7 & 8 is obtained.

Sometimes, it may be possible to find more than two pairs of lines such that the sum of the frequencies (with respect to $\frac{1}{2}(\nu_A + \nu_B)$) of each pair is equal to

$[(\nu_0\delta)^2+N^2]^{1/2}$ within experimental error. Then among these pairs, two should be chosen such that the observed spectrum is properly accounted for.

Some trial and error calculations are, therefore, necessary to decide upon the proper assignment. Further, at two stages in the above procedure, firstly for the identification of lines 1 and 3 and secondly for deciding the proper roots E_3 and E_4, a knowledge of approximate values of the coupling constants is said to be necessary. This, however, does not place any drastic limitation on the method (except that more trial and error calculations may be necessary) as any particular assignment is ultimately checked completely for internal consistency.

After satisfactorily assigning lines 1 to 8, if some lines in the observed spectrum are still left unassigned, they may be assigned properly to transitions 9 to 12 and the value of M may then be calculated. However, it may be noted that the value of M is very sensitive to slight errors in the line position (even within the limits of experimental error), and therefore, an approximate value of M may be estimated such that the calculated frequency agrees with the observed frequency, within experimental error. It is usually difficult to determine the sign of M, as this can only be done if the intensities

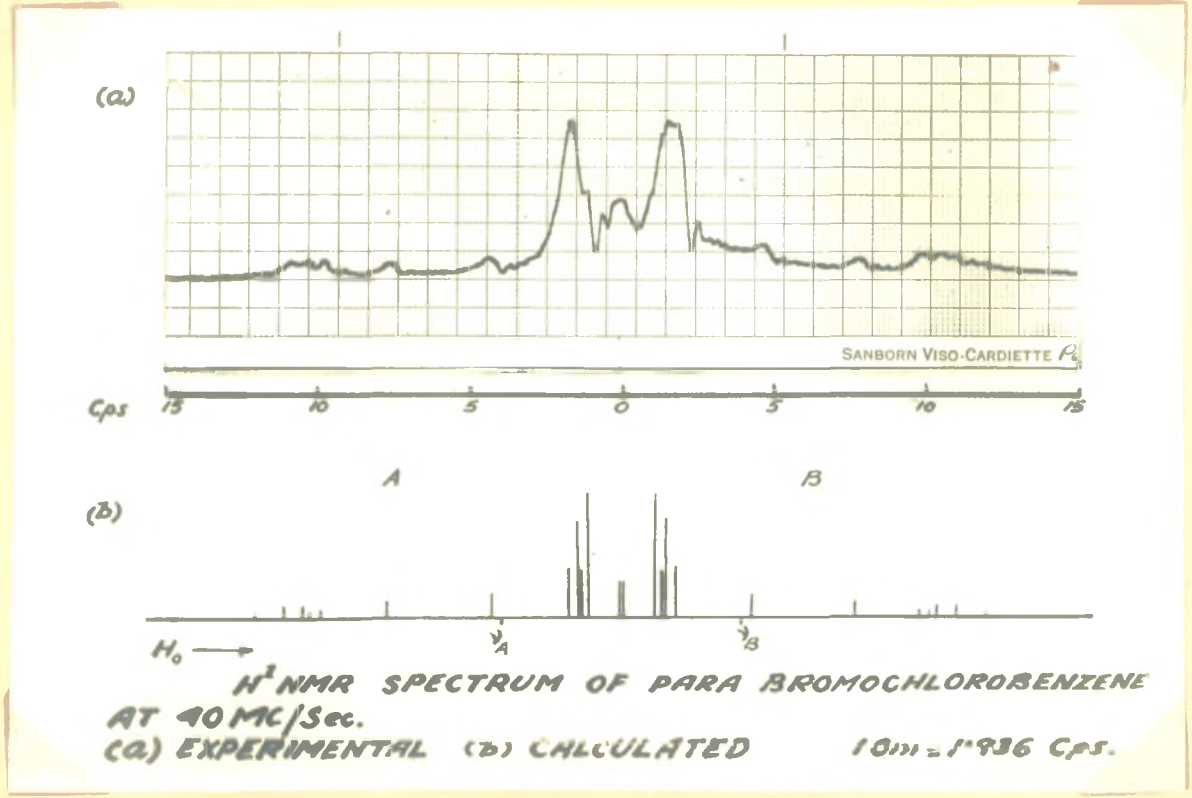
are accurately known. So, it cannot be found which of the two meta H-H coupling constants (J_A and J_B) is larger.

The relative signs of the coupling constants cannot be determined in this analysis and all the coupling constants are assumed to be positive for the spectra analysed.

(iv) P - Bromochlorobenzene:

Following the above method, the lines at 1.50cps and 10.40cps with respect to the center of the spectrum (Fig III.2(a)) are assigned to the transitions 3 and 1 respectively. From this we obtain N = 8.9cps and $\left[(\nu_0\delta)^2+N^2\right]^{1/2}$ = 11.9cps. The two lines at 4.30 and 7.70cps are assigned to the transitions 6 and 7, and the line at 0cps is taken as one of the two transitions 5 and 8 (Even if one of the pair of lines is identified the corresponding root of the Eqn. (III.2) can be determined). The lines at 10.91 and 1.10 also appear to be a plausible pair of lines to be assigned to either the transitions 6 & 7 or 5 & 8. But, this was finally discarded as the assignment on this basis does not account for the line at 0cps.

The parameters obtained in the analysis are given in Table III.5. The line frequencies and relative



H^1 NMR SPECTRUM OF PARA BROMOCHLOROBENZENE AT 40 MC/Sec.
(a) EXPERIMENTAL (b) CALCULATED $10^{III} = 1^{\cdot}936$ Cps.

Fig. III. 2.

TABLE-III.2.

Calculated transition frequencies and relative intensities, and observed frequencies for P-bromochlorobenzene.

Transition No.*	Calculated frequency (in cps.)	Observed frequency † (in cps.)	Calculated Relative Intensity
5	11.90	---	0.05
2	11.06	10.91	0.21
1	10.40	10.40	0.25
9	10.16		0.13
10	9.79	9.81	0.15
6	7.65	7.70	0.29
7	4.25	4.30	0.42
11	1.74		0.87
3	1.50	1.50	1.75
12	1.37		0.85
4	1.11	1.10	2.23
8	0.00	0.00	0.61

(Calculated and observed frequencies are given for a half of the spectrum with respect to the center $\frac{1}{2}(\nu_A+\nu_B)$.

* Nos. as in Table III.1.

† Standard deviation vary between 0.07 and 0.15cps.

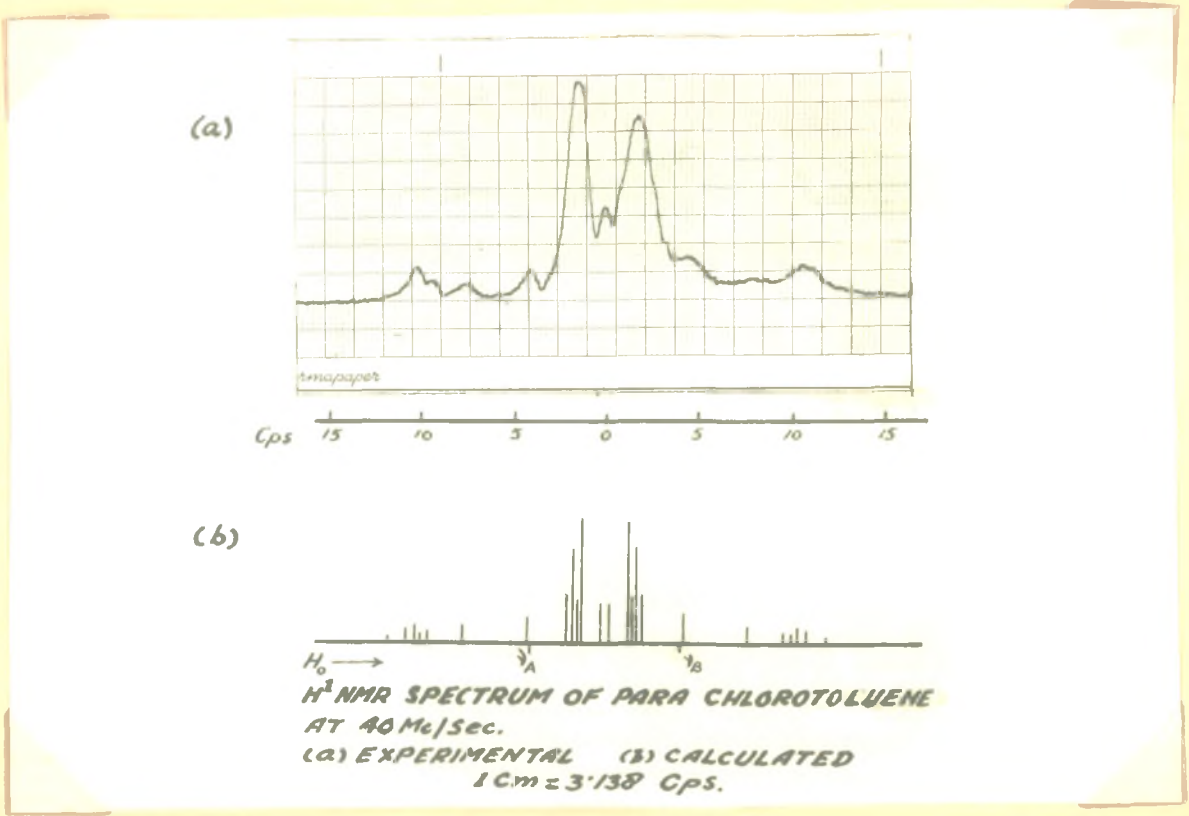
intensities calculated on the basis of these parameters are given in Table III.2, along with the experimentally observed line frequencies. The calculated spectrum is shown in Fig. III.2 (b).

The parameters (Table III.5) are all given assuming that $\nu_A > \nu_B$, but it is not possible to identify from this analysis, which pair of nuclei are shielded more.

The half of the observed spectrum on the higher field side shows less detail in the structure and this is presumably due to spin-spin coupling with either bromine or chlorine nucleus, which results in a broadening of the lines due to quadrupole interactions. Irradiating these nuclei (Br or Cl) with a strong RF voltage of appropriate frequency, while observing proton resonance might reveal more structure in these lines. By this method it may then be possible to determine which pair of nuclei give rise to this half of the spectrum.

(v) Para Chlorotoluene:

The analysis of this spectrum is done in the same manner as for p-bromochlorobenzene, and the parameters obtained (assuming $\nu_A > \nu_B$) are given in Table III.5.



H^1 NMR SPECTRUM OF PARA CHLOROTOLUENE AT 40 Mc/Sec.
(a) EXPERIMENTAL (b) CALCULATED
1 C.m = 3·138 Cps.

Fig. III · 3.

TABLE III.3.

Calculated transition frequencies and relative intensities, and observed frequencies for p-chlorotoluene.

Transition No.*	Calculated frequency (in cps.)	Observed frequency † (in cps.)	Calculated Relative Intensity
5	11.82	—	0.07
2	10.78		0.24
1	10.36	10.36	0.28
9	9.97		0.14
10	9.61	9.41	0.17
6	7.71	7.73	0.32
7	4.31	4.33	0.46
11	1.93		0.86
3	1.66	1.66	1.72
12	1.57		0.83
4	1.27		2.22
8	0.20	0.20	0.72

(Calculated and observed frequencies are given for a half of the spectrum with respect to the center $\frac{1}{2}(\nu_A+\nu_B)$).

* Nos. as in Table III.1.

† Standard deviations vary between 0.04 and 0.09 cps.

The lines in the half of the spectrum on the higher field side show certain broadening in this case also, probably for the same reasons as given for p-bromochlorobenzene. The double irradiation technique might be helpful in this case also to determine which pair of nuclei are shielded more.

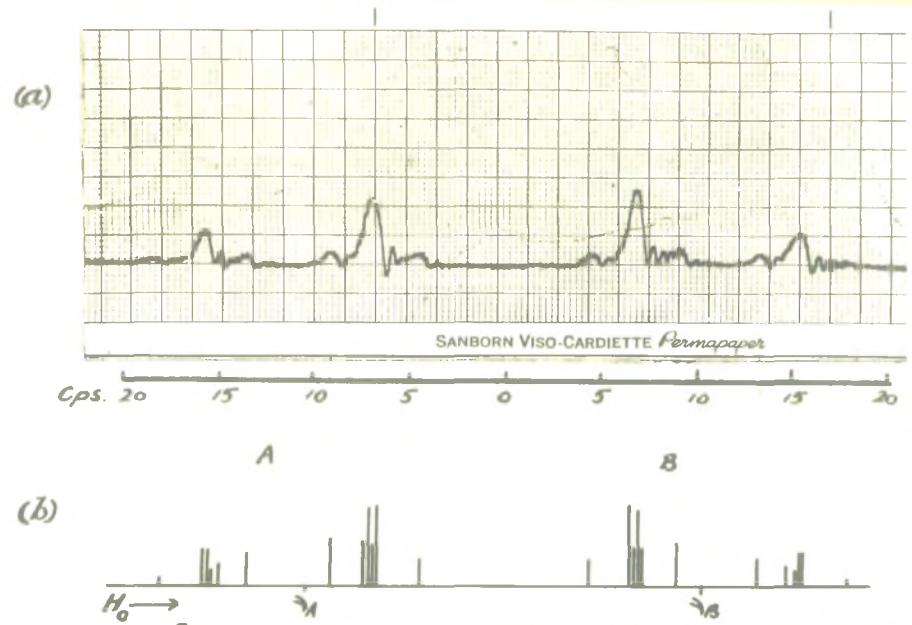
The line frequencies and relative intensities calculated on the basis of the parameters in Table III.5, are given in Table III.3, along with the observed frequencies. The calculated spectrum is shown in Fig.III.3 (b).

(vi) P-Chloroiodobenzene:

The analysis is done on identical lines as for the other two molecules, and the parameters obtained are given in Table III.5.

By comparing with the results obtained by Corio and Bailey (4) on the chemical shifts in the monosubstituted benzenes, the two protons ortho to iodine may be expected to be shielded less in this case.

The line frequencies and the relative intensities calculated on the basis of the parameters in Table III.5, are given in Table III.4 along with the observed line frequencies. The calculated spectrum is shown in Fig.III.4 (b).



H^1 NMR SPECTRUM OF PARA CHLOROIODO-BENZENE AT 40 Mc/Sec.
(a) EXPERIMENTAL (b) CALCULATED
1 Cm = 3·184 Cps.

Fig. III. 4.

TABLE III.4.

Calculated transition frequencies and relative intensities, and observed frequencies for p-chloroiodobenzene.

Transition No.*	Calculated frequency † (in cps.)	Observed frequency # (in cps.)	Calculated Relative Intensity
5	18.02	18.07	0.13
2	15.65	15.60	0.60
1	15.60		0.61
9	15.42		0.30
10	14.96		0.34
6	13.45	13.50	0.56
7	9.05	9.10	0.82
11	7.31	6.89	0.70
3	6.89		1.39
12	6.84		0.66
4	6.68		1.45
8	4.48	4.53	0.47

(Calculated and observed frequencies are given for a half of the spectrum with respect to the center $\frac{1}{2}(\nu_A+\nu_B)$).

* Nos. as in Table III.1.

† The value of H is assumed to be 0.5cps in comparison with the other two molecules.

Standard deviations vary between 0.06 and 0.19cps.

TABLE III.5.

Values of the parameters* obtained from the analyses (The values obtained by RS† (3) are given for comparison).

Compound	$\nu_0\delta$	J_o^{HH}	J_m^{HH}		J_p^{HH}
			1	2	
1. P-bromochlorobenzene	7.9	8.65	2.3	2.4	0.25
Values of RS	7.1	9.1	(Range 1.5-2.0)		0
2. P-chlorotoluene	8.3	8.35	2.7	2.2	0.35
Values of RS	5.3	9.1	(Range 1.5-2.0)		0
3. P-chloroiodobenzene	20.7	8.4	2.7	2.2	0.3
Values of RS	20.8	9.0	1.6		0

* The values are all given in cps. The error involved in any of the parameters is about ± 0.2cps.

† The $\nu_0\delta$ values in reference(3)are multiplied by (40/29.92) to compare with the values in the present work.

(vii) Discussion:

The agreement between the calculated and observed spectra for all the three cases is satisfactory, as seen from Tables III.2, III.3 & III.4, and Figs. III.2, III.3, III.4 and the method of analysis, therefore, appears to be reliable.

The corresponding values of the parameters obtained by RS in all these cases are also shown in Table III.5 for comparison.

The ortho coupling constants (J_o^{HH}) obtained by RS are all larger than the values obtained here. This is because of the assumption made by RS that J'=0, and the value of J_o^{HH} determined by them corresponds to 'K' in the present analysis.

All the meta H-H coupling constants (J_m^{HH}) obtained here are outside the range of 1.5 to 2.0cps suggested by RS for these molecules. But RS have chosen different zero order eigenfunctions for the states $3s_o$ and $4s_o$, and so the fourth power equation determining the energy values corresponding to the states $1s'_o$, $2s'_o$, $3s'_o$, & $4s'_o$, in their case, is different from Eq. (III.2). The reason for so choosing these zero order eigenfunctions is not clear from their publication (3). The discrepancy

in the values of J_m^{HH} obtained by them may be traced to this reason.

All the coupling constants observed here, agree with the values of the ortho, meta and para H-H coupling constants in substituted benzenes determined by earlier workers.

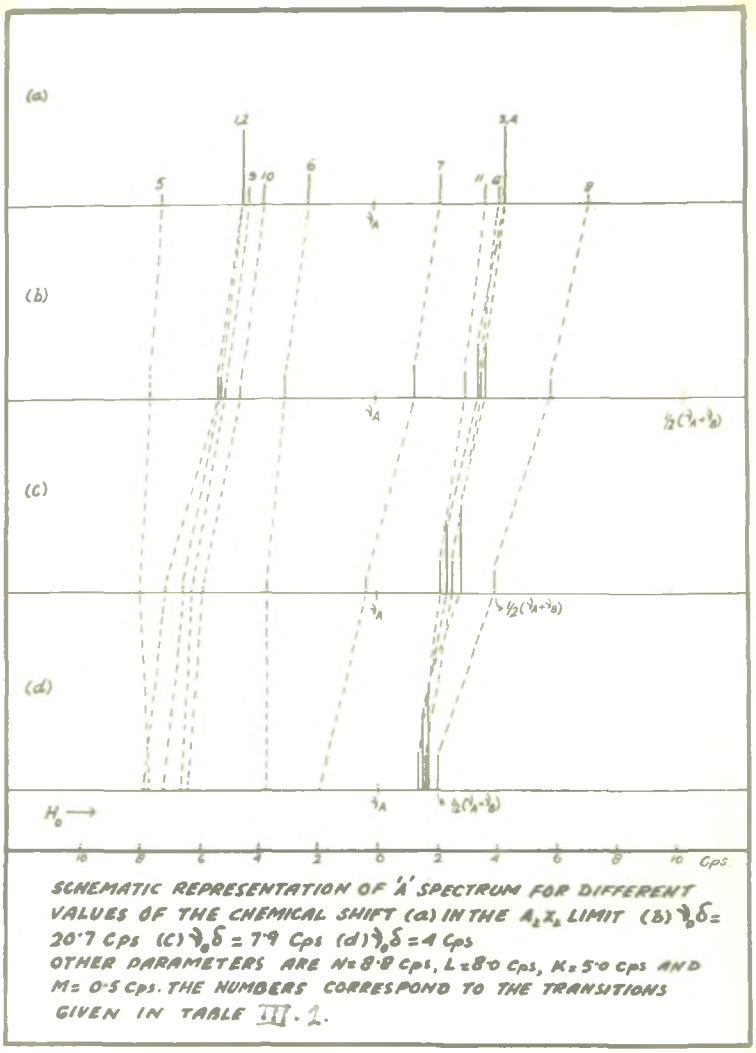
The value of $\nu_0\delta$ for p-chloroiodo benzene obtained here agrees ~~well~~ with the value of RS very closely (Table III.5). However, there is considerable discrepancy between the $\nu_0\delta$ values determined here and those of RS (converted to 40 Mc/Sec. as given in Table III.5) in the case of p-bromochlorobenzene and p-chlorotoluene. The value of $\nu_0\epsilon$ is small in both these cases, and it is smaller still at 29.92 Mc/Sec. used by RS for the work. The assignment of the lines to the transitions is usually rendered difficult when $\nu_0\delta$ is small and this is probably the reason for the low values of $\nu_0\delta$ obtained by RS in these cases. As the present experiments are done at 40 Mc/Sec. the values reported here are more reliable than those of RS.

The results obtained (Table III.5) show that the spin-spin coupling constants are not much sensitive to substitution. The same conclusion has also been reached by RS.

(viii) Dependence of the Spectrum on the Chemical Shift:

In view of the several difficulties involved in arriving at a correct assignment, it is thought worthwhile to calculate the spectra for some typical values of $\nu_0\delta$ as the rest of the parameters remain approximately the same for all the p-disubstituted benzenes. The manner in which a typical half of the spectrum varies with $\nu_0\delta$ is schematically represented in Fig. III.5. In the limit when $\nu_0\delta$ is large compared to the coupling constants (A_2X_2 case) the half of the spectrum is again symmetrical in the positions of the lines as well as the intensities about the center ν_A. As $\nu_0\delta$ decreases the spectrum becomes gradually unsymmetrical with respect to the center (ν_A) and the intensity of the lines nearer to $\frac{1}{2}(\nu_A+\nu_B)$ increases, whereas the lines away from $\frac{1}{2}(\nu_A+\nu_B)$ diminish in intensity and some of them may even escape detection at small values of $\nu_0\delta$. The spectra (b) and (c) in Fig. III.5 are the same as those of p-chloroiodobenzene and p-bromochlorobenzene respectively. The spectrum (d) in Fig III.5 is calculated for $\nu_0\delta$ =4.0cps. Other parameters used in the calculation are

$$\left.\begin{array}{ll} K = 5.0\text{cps} & N = 8.5\text{cps} \\ M = 0.5\text{cps} & L = 8.0\text{cps} \end{array}\right\} \qquad \text{(III.4)}$$



SCHEMATIC REPRESENTATION OF 'A' SPECTRUM FOR DIFFERENT VALUES OF THE CHEMICAL SHIFT (a) IN THE A_2X_2 LIMIT (b) $\nu_0\delta$ = 20·7 cps (c) $\nu_0\delta$ = 7·9 cps (d) $\nu_0\delta$ = 4 cps OTHER PARAMETERS ARE N = 8·8 cps, L = 8·0 cps, K = 5·0 cps AND M = 0·5 cps. THE NUMBERS CORRESPOND TO THE TRANSITIONS GIVEN IN TABLE III. 2.

Fig. III. 5.

TABLE III.6.

Typical half of A_2B_2 spectrum calculated for the parameters,

$\nu_0\delta$ =4.0cps, J=8.5cps, L=8.0cps, K=5.0cps,
and M=0.5cps.

Transition No.*	Transition frequency w.r.t. $\frac{1}{2}(\nu_A+\nu_B)$ in cps.		Relative Intensity
1.	9.23	..	0.09
2.	9.93	..	0.07
3.	0.43	..	1.91
4.	0.27	..	2.82
7.	3.92	..	0.08
8.	-0.05	..	0.88
5.	9.71	..	0.025
6.	5.74	..	0.12
9.	8.60	..	0.05
10.	8.37	..	0.06
11.	0.58	..	0.95
12.	0.36	..	0.94

* Nos. as in Table III.1.

The line frequencies and the relative intensities for this case$ are given in Table III.6.

It can be seen from Fig. III.5 that the spectrum depends on the chemical shift in a rather complicated manner, but the schematic variation shown in this diagram may be useful in analysing the spectra of this type.

REFERENCES.

1. Pople. J. A., Schneider. W. G. and Bernstein. H. J., Can. J. Chem. 35, 1060, (1957).

2. Pople, J. A., Schneider. W. G. and Bernstein. H. J., "High Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., Inc., New York, (1959).

3. Richards. R. E. and Schaeffer. T. P., Trans. Farad. Soc. 54, 1280, (1958).

4. Corio. P. L. and Dailey. B. P., J. Am. Chem. Soc. 78, 3043, (1956).

CHAPTER IV.

PROTON RESONANCE SPECTRA OF α, β AND γ PICOLINES

PROTON RESONANCE SPECTRA OF α, β AND γ PICOLINES.

A B S T R A C T.

The proton resonance spectra of α, β and γ picolines are obtained and analyzed to determine all the parameters involved. The spectra belong to the classes ABCX, ABXY and A_2X_2 respectively. The parameters obtained in all these cases do not differ very much from the corresponding parameters in pyridine spectrum analyzed by Schneider et.al.

(1) Introduction:

The proton resonance spectra of pyridine and some methyl substituted pyridines (picolines and lutidines) were studied earlier by Baker (1) and Bernstein and Schneider (2). These were done at low resolution (about 1 in 10^7) and were not therefore completely analyzed to determine all the parameters. Schneider, Bernstein and Pople (3) have recently studied the spectra of pyridine and some deutorated pyridines under high resolution (about 1 in 10^8) and obtained all the parameters involved by an exact analysis.

In the present experiments the proton resonance spectra of α, β and γ picolines are studied at 40 Mc/Sec. under a resolution of about 1 in 10^8. The spectra are of the types ABCX, ABXY and A_2X_2 respectively. All three spectra are analyzed and the involved parameters are determined.

(ii) Experimental:

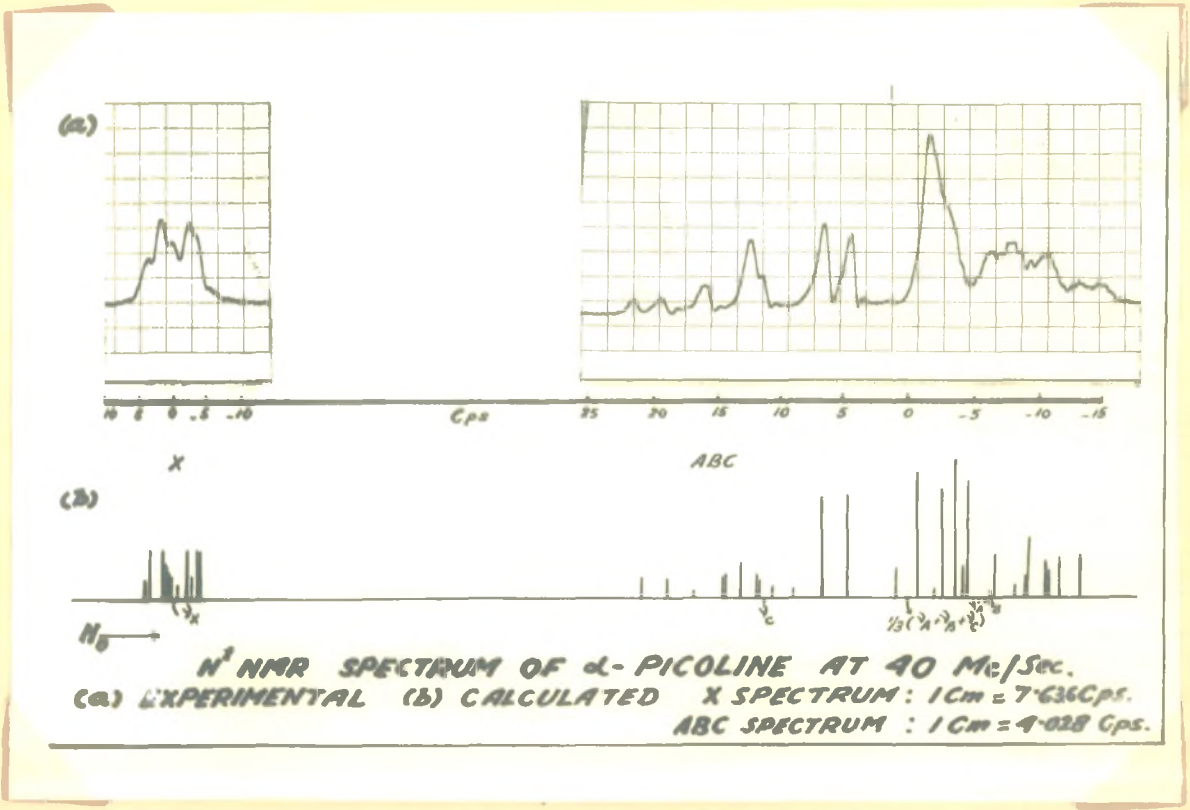
The samples of α, β and γ picolines are kindly provided by Dr. H. Sripathi Rao, Central Fuel Research Institute, Jealgora. Slight traces of other isomers and some absorbed moisture are the probable impurities in the samples (4).

The absolute chemical shifts of the resonance signals are measured, choosing water as an external standard in the form of a capillary placed inside the main sample tube.

The resonance of the methyl protons occurs at a higher field than that of the ring protons in all the cases. This signal does not show any splitting in any of the three compounds indicating that the coupling of the ring protons with the methyl protons, if any, is small.

(iii) α-Picoline:

The ring proton spectrum of the molecule, shown in Fig. IV.1(a), contains two groups of lines separated by about 60 cps. By comparing with the pyridine spectrum(3) and by an approximate measurement of the areas enclosed by the two groups of lines, the group of lines at the lower field may be assigned to the proton 6 (Fig. IV.2). As the



N^1 NMR SPECTRUM OF α-PICOLINE AT 40 Mc/Sec.
(a) EXPERIMENTAL (b) CALCULATED X SPECTRUM : 1 Cm = 7·636 Cps.
ABC SPECTRUM : 1 Cm = 4·028 Cps.

Fig. IV . 1.

resonance of this proton is well separated from that of the other three protons, this four spin system may be taken as belonging to the ABCX type.

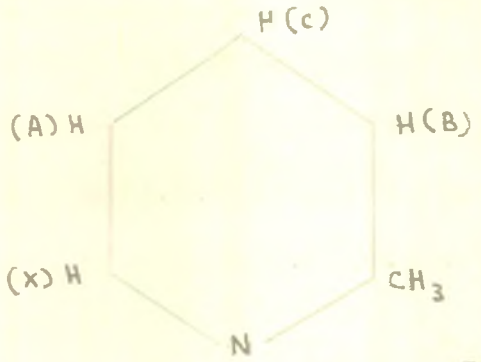


Fig IV.2

The zero order eigenfunctions and the corresponding diagonal matrix elements for the ABCX system are given in Table II.1. The non-vanishing off-diagonal elements are given in Eq. (II.1). It is necessary to diagonalise four 3 x 3 matrices in order to obtain all the energy levels and, therefore, explicit analytical expressions are not usually obtained for the transition energies. Hence, the assignment of the observed lines to different transitions cannot be done in a simple and direct manner.

A comparison of the lines at the lower field with the lines due to ortho protons in the spectrum of pyridine (3) shows that the multiplet structure of this group of lines remains practically unchanged, and the mutual separations between these lines are also nearly the same. This indicates, firstly, that the coupling between the ortho protons in pyridine is small (This

is actually found to be so by Schneider et.al (3)) and, secondly, that the coupling constants J_{AX}, J_{BX} & J_{CX} in α-picoline do not differ much from the corresponding coupling constants in pyridine. In view of this, it is first, tentatively, assumed that all the parameters involved in this spectrum are roughly the same* as the corresponding parameters in pyridine. They are given by

$$\left.\begin{aligned} &\nu_0\delta_{AB} = 0 \text{ cps.} && J_{AC} = J_{BC} = 7.5 \text{ cps.} \\ &\nu_0\delta_{AC} = -15 \text{ cps.} && J_{AB} = 1.6 \text{ cps.} \\ & && J_{AX} = 5.5 \text{ cps.} \\ & && J_{BX} = 0.9 \text{ cps.} \\ & && J_{CX} = 1.9 \text{ cps.} \end{aligned}\right\} \quad \text{(IV.1)}$$

On the basis of these parameters, the transition energies and relative intensities are calculated for the ABCX system. Though the spectrum, thus calculated, does not fit in the observed spectrum correctly, a general resemblance is observed from which a rough idea of the probable positions of the involved transitions is obtained. The calculations, along with a rough measurement of the areas, showed that in the observed spectrum assigned to the protons AB & C, the seven lines on the

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* The chemical shifts are also assumed to be the same, in the first instance, as methyl substitution is not expected to alter these drastically.

low field side arise due to the proton C. Then, it can be seen that the lines of the protons A & B are not sufficiently resolved as there are only 6 or 7 distinguishable peaks in this part of the spectrum while the number of transitions are about twenty.

Using these calculations as a starting point, it is attempted to assign the different lines to particular transitions by trial and error. The following points are of considerable help in deciding upon the assignment.

As the off-diagonal elements in a matrix are applied adiabatically in the process of diagonalization (a) the trace of the matrix remains the same, and (b) the diagonal elements will not cross each other. If we express the frequency of a transition between states $m \rightarrow n$ as $\nu_{mn} = E_n - E_m$, we have that *

$$\nu_{31} + \nu_{41} + \nu_{51} = 3E_1 - (E_3 + E_4 + E_5) \qquad \text{(IV.2)}$$

and as $(E_3 + E_4 + E_5)$ is the trace of the matrix which determines the energy levels 3', 4', & 5' we find from Table II.1 that

$$\nu_{31} + \nu_{41} + \nu_{51} = (\nu_A + \nu_B + \nu_C) + (J_{AB} + J_{BC} + J_{AC}) + \tfrac{1}{2}(J_{AX} + J_{BX} + J_{CX})$$

$$= \Sigma \nu_n + \Sigma J_{AB} + \tfrac{1}{2}\Sigma J_{AX} \quad \cdots \quad \text{(IV.3)}$$

---

* The procedure has been used earlier by Fessenden and Waugh (5) in the analysis of ABC spectra.

Similarly we find that

$$\nu_{62} + \nu_{72} + \nu_{82} = \Sigma \nu_A + \Sigma J_{AB} - \tfrac{1}{2} \Sigma J_{AX} \quad \cdots (\text{IV}.4)$$

$$\nu_{15,9} + \nu_{15,10} + \nu_{15,11} = \Sigma \nu_A - \Sigma J_{AB} + \tfrac{1}{2} \Sigma J_{AX} \quad \cdots (\text{IV}.5)$$

$$\nu_{16,12} + \nu_{16,13} + \nu_{16,14} = \Sigma \nu_A - \Sigma J_{AB} - \tfrac{1}{2} \Sigma J_{AX} \quad \cdots (\text{IV}.6)$$

If the twelve transitions occuring in Eqns. (IV.3) to (IV.6) are assigned to the lines in the observed spectrum, the three quantities $\Sigma \nu_A$, ΣJ_{AB} and ΣJ_{AX} are easily obtained. $\Sigma \nu_A$, however, depends on the choice of origin in the observed spectrum, but it can be used to find the position of $\frac{1}{3}(\nu_A + \nu_B + \nu_C)$ in the spectrum. This position may then be fixed as the new origin to express all the transition frequencies in the theoretical, as well as experimental spectra.

For the X transitions of the following relations are easily obtained.

$$\left.\begin{aligned} \nu_{21} &= \nu_x + \tfrac{1}{2} \Sigma J_{AX} \\ \nu_{16,15} &= \nu_x - \tfrac{1}{2} \Sigma J_{AX} \\ \nu_{63} + \nu_{74} + \nu_{85} &= 3\nu_x + \tfrac{1}{2} \Sigma J_{AX} \\ \nu_{12,9} + \nu_{13,10} + \nu_{14,11} &= 3\nu_x - \tfrac{1}{2} \Sigma J_{AX} \end{aligned}\right\} \quad \cdots \quad (\text{IV}.7)$$

The position of ν_x in the observed spectrum and the value of ΣJ_{AX} might be calculated if these transitions are properly assigned, and the value of ΣJ_{AX}, thus obtained, can be checked with that determined from the assignment of ν_{21} etc.

transitions ν_{31} etc. In the present case the lines due to X proton are not well resolved and the line widths are rather large so that the assignment ca not be done properly.

After the twelve transitions occuring in Eqns. (IV.3) to (IV.6) are assigned, all the energy levels are calculated from the assigned frequencies of these transitions (and from the values of ΣJ_{AB} & ΣJ_{AX} obtained from them). The remaining 18 transitions in the ABC spectrum are then calculated and checked with the observed spectrum. The intensities of the corresponding transitions in the theoretical spectrum calculated with the parameters in Eq. (I V.1) are of help in making this comparison. The agreement between the calculated and observed spectrum corresponding to the 18 transitions forms a check on the correctness of the assignment of transitions ν_{31} etc.

If the observed spectrum (of all the four protons ABC & X) is satisfactorily accounted for, the problem would then be to obtain all the involved parameters from the energy values which account for the spectrum. This, again, cannot be done by analytical method and, therefore, a numerical method is followed. For this, different sets of values are chosen, within a reasonable range close to the corresponding values in pyridine, for all the parameters (and also remembering

that ΣJ_{AB} & ΣJ_{AX} are known) and the energy levels given by all these sets are calculated. The set of parameters which yield energy values that fit with those obtained from the above assignment is finally chosen.

The parameters thus chosen are

$$\left.\begin{array}{ll} \gamma_o \delta_{AB} = 0.5 \text{ cps.} & J_{AB} = 1.0 \text{ cps.} \\ \gamma_o \delta_{BC} = -17.0 \text{ cps.} & J_{BC} = 7.4 \text{ cps.} \\ \gamma_o \delta_{AC} = -16.5 \text{ cps.} & J_{AC} = 7.4 \text{ cps.} \\ & J_{AX} = 4.5 \text{ cps.} \\ & J_{BX} = 0.6 \text{ cps.} \\ & J_{CX} = 2.0 \text{ cps.} \end{array}\right\} \quad \text{(IV.8)}$$

It may be noted that the energy values are considerably sensitive to small changes in the parameters and though the agreement finally obtained is satisfactory it cannot be claimed that the set of values in Eqn. (IV.8) represent the best values of <u>all</u> the eight parameters. Further refinement of these values is discouraged by the fact that there are several unresolved lines in the spectrum. However, it can be said that within reasonable limits of about ± 0.5 cps. in the coupling constants and about ±1.0 cps. in the chemical shifts the set of parameters in Eqn. (IV.8) represent the spectrum.

The exact wave functions corresponding to the energy values are calculated with the help of Eqns.(I.5), (I.6) & (I.7) and the relative intensities of the

$$\left.\begin{aligned}
&\tfrac{1}{2}\left[(J_{AX}+J_{BX})+(J_{AY}+J_{BY})\right]\\
&\tfrac{1}{2}\left[(J_{AX}+J_{BX})-(J_{AY}+J_{BY})\right]\\
&\tfrac{1}{2}\left[-(J_{AX}+J_{BX})+(J_{AY}+J_{BY})\right]\\
&\tfrac{1}{2}\left[-(J_{AX}+J_{BX})-(J_{AY}+J_{BY})\right]
\end{aligned}\right\} \cdots (IV.11)$$

and from these $(J_{AX} + J_{BX})$ and $(J_{AY} + J_{BY})$ are obtained. Thus, all the parameters except δ_{xy} can be derived from the analysis of the AB spectrum. It is, however, not possible to derive the signs of coupling constants from this analysis, as is done in the case of 1 fluoro, 2,4-dinitrobenzene, as no information is obtained from the X and Y lines in this case.

The analysis is therefore carried out assuming all the coupling constants to be positive.

The parameters obtained from the analysis are

$$\left.\begin{aligned}
\nu_o\delta_{AB} &= 10.3 \text{ cps.} & J_{AB} &= 7.9 \text{ cps.}\\
\nu_o\delta_{xy} &= 44.3 \text{ cps.} & J_{AX} &= 1.7 \text{ cps.}\\
& & J_{BX} &= 4.8 \text{ cps.}\\
& & J_{AY} &= 2.5 \text{ cps.}\\
& & J_{BY} &= 1.2 \text{ cps.}\\
& & J_{XY} &= 0 \text{ cps.}
\end{aligned}\right\} \cdots (IV.12)$$

The error involved in any of these parameters is not more than $\pm$ 0.4 cps.

TABLE IV.1.

Exact wave functions and energy levels of α - picoline.

Sl. No.	F_z	Wave function ϕ_n †	Energy E_n
1'	2	ϕ_1^0	$\frac{1}{2}(\gamma_A+\gamma_B+\gamma_C+\gamma_X)$ + 5.725
2	1	ϕ_2^0	$\frac{1}{2}(\gamma_A+\gamma_B+\gamma_C-\gamma_X)$ + 2.175
3'	1	−0.97 ϕ_3^0 +0.16 ϕ_4^0 +0.18 ϕ_5^0	$\frac{1}{6}(\gamma_A+\gamma_B+\gamma_C+3\gamma_X)$ −15.097
4'	1	0.20 ϕ_3^0 +0.90 ϕ_4^0 +0.37 ϕ_5^0	$\frac{1}{6}(\gamma_A+\gamma_B+\gamma_C+3\gamma_X)$ + 8.265
5'	1	0.14 ϕ_3^0 −0.28 ϕ_4^0 +0.95 ϕ_5^0	$\frac{1}{6}(\gamma_A+\gamma_B+\gamma_C+3\gamma_X)$ + 4.656
6'	0	−0.97 ϕ_6^0 +0.17 ϕ_7^0 +0.16 ϕ_8^0	$\frac{1}{6}(\gamma_A+\gamma_B+\gamma_C-3\gamma_X)$ −16.639
7'	0	−0.07 ϕ_6^0 −0.87 ϕ_7^0 +0.49 ϕ_8^0	$\frac{1}{6}(\gamma_A+\gamma_B+\gamma_C-3\gamma_X)$ + 4.131
8'	0	0.22 ϕ_6^0 +0.46 ϕ_7^0 +0.86 ϕ_8^0	$\frac{1}{6}(\gamma_A+\gamma_B+\gamma_C-3\gamma_X)$ + 6.783
9'	0	0.96 ϕ_9^0 −0.20 ϕ_{10}^0 −0.21 ϕ_{11}^0	$-\frac{1}{6}(\gamma_A+\gamma_B+\gamma_C-3\gamma_X)$ − 6.042
10'	0	0.15 ϕ_9^0 +0.95 ϕ_{10}^0 −0.26 ϕ_{11}^0	$-\frac{1}{6}(\gamma_A+\gamma_B+\gamma_C-3\gamma_X)$ − 8.505
11'	0	0.26 ϕ_9^0 +0.22 ϕ_{10}^0 +0.94 ϕ_{11}^0	$-\frac{1}{6}(\gamma_A+\gamma_B+\gamma_C-3\gamma_X)$ + 8.822
12'	−1	0.89 ϕ_{12}^0 +0.36 ϕ_{13}^0 −0.29 ϕ_{14}^0	$-\frac{1}{6}(\gamma_A+\gamma_B+\gamma_C+3\gamma_X)$ − 7.574
13'	−1	0.05 ϕ_{12}^0 +0.96 ϕ_{13}^0 −0.28 ϕ_{14}^0	$-\frac{1}{6}(\gamma_A+\gamma_B+\gamma_C+3\gamma_X)$ − 5.026
14'	−1	0.23 ϕ_{12}^0 +0.26 ϕ_{13}^0 +0.94 ϕ_{14}^0	$-\frac{1}{6}(\gamma_A+\gamma_B+\gamma_C+3\gamma_X)$ +10.425
15	−1	ϕ_{15}^0	$-\frac{1}{2}(\gamma_A+\gamma_B+\gamma_C-\gamma_X)$ + 2.175
16	−2	ϕ_{16}^0	$-\frac{1}{2}(\gamma_A+\gamma_B+\gamma_C+\gamma_X)$ + 5.725

† ϕ_n^0 are the zero order eigenfunctions as given in Table II.1.

TABLE IV.2.

Calculated transition frequencies and relative intensities, and observed frequencies for ∝-picoline.

S.No.	Transition	Calculated frequency (in cps.)	Observed frequency† (in cps.)	Calculated Relative Intensity
ABC lines				
1.	3' → 1	20.8	21.0	0.40
2.	6' → 2	18.8	18.9	0.41
3.	10' → 4'	16.8		0.14
4.	12' → 8'	14.4	15.3	0.37
5.	9' → 4'	14.3		0.46
6.	10' → 5'	13.2		0.71
7.	13' → 8'	11.8		0.49
8.	12' → 7'	11.7	12.0, 10.9	0.33
9.	9' → 5'	10.7		0.24
10.	13' → 7'	9.2		0.21
11.	15 → 11'	6.7	6.3	2.02
12.	16 → 14'	4.7	4.3	2.04
13.	5' → 1	1.1		0.66
14.	11' → 4'	-0.6	-1.9,	2.58
15.	7' → 2	-2.0		0.20

Contd..

TABLE IV.2 (Contd.)

S.No.	Transition	Calculated frequency (in cps.)	Observed frequency (in cps.)	Calculated Relative Intensity
16.	4' → 1	-2.5		2.16
17.	14' → 8'	-3.6	-1.9,	2.82
18.	11' → 5'	-4.2	-3.4	0.69
19.	8' → 2	-4.6		2.37
20.	14' → 7'	-6.3	-6.2	0.22
21.	10' → 3'	-6.5		0.92
22.	15 → 9'	-8.2		0.30
23.	9' → 3'	-9.0	-8.0	0.48
24.	12' → 6'	-9.1		1.21
25.	15 → 10'	-10.7	-10.5,	0.71
26.	16 → 13'	-10.8	-13.1,	0.53
27.	13' → 6'	-11.6	-14.8?	0.85
28.	16 → 12'	-13.3		0.92
29.	11' → 3'	-23.9	—	0.0042
30.	14' → 6'	-27.1	—	0.0071
X Lines				
1.	6' → 4'	24.0	—	0.0009
2.	6' → 5'	21.3	—	0.001
3.	12' → 11'	16.4	—	0.001
4.	13' → 11'	13.9	—	0.002

Contd..

TABLE IV.2. (Contd.)

S.No.	Transition	Calculated frequency (in cps.)	Observed frequency (in cps.)	Calculated Relative Intensity
5.	7' → 4'	4.1	4.1	0.38
6.	2 → 1	3.6	2.0, 0.5	1.00
7.	6' → 3'	1.5		0.99
8.	12' → 9'	1.5		0.71
9.	8' → 4'	1.5		0.60
10.	7' → 5'	0.5		0.49
11.	12' → 10'	-0.9	-1.9	0.30
12.	13' → 9'	-1.0		0.007
13.	14' → 11'	-1.6		1.00
14.	8' → 5'	-2.1		0.52
15.	13' → 10'	-3.5	-3.5	0.98
16.	16 → 15	-3.6		0.46
17.	14' → 9'	-16.5	—	0.0003
18.	14' → 10'	-18.9	—	0.0001
19.	7' → 3'	-19.2	—	0.0002
20.	8' → 3'	-21.9	—	0.0002

† Standard deviations vary between 0.17 and 0.27 cps.

Values of Chemical shifts (δ) for the different protons with respect to the signal from water:— (The values are corrected for bulk diamagnetic susceptibility).

Type of proton*		δ w.r.t. H_2O in ppm
A	...	-1.70 ±0.02
B	...	-1.69 "
C	...	-2.12 "
X	...	-3.26 "
CH_3	...	2.81 "

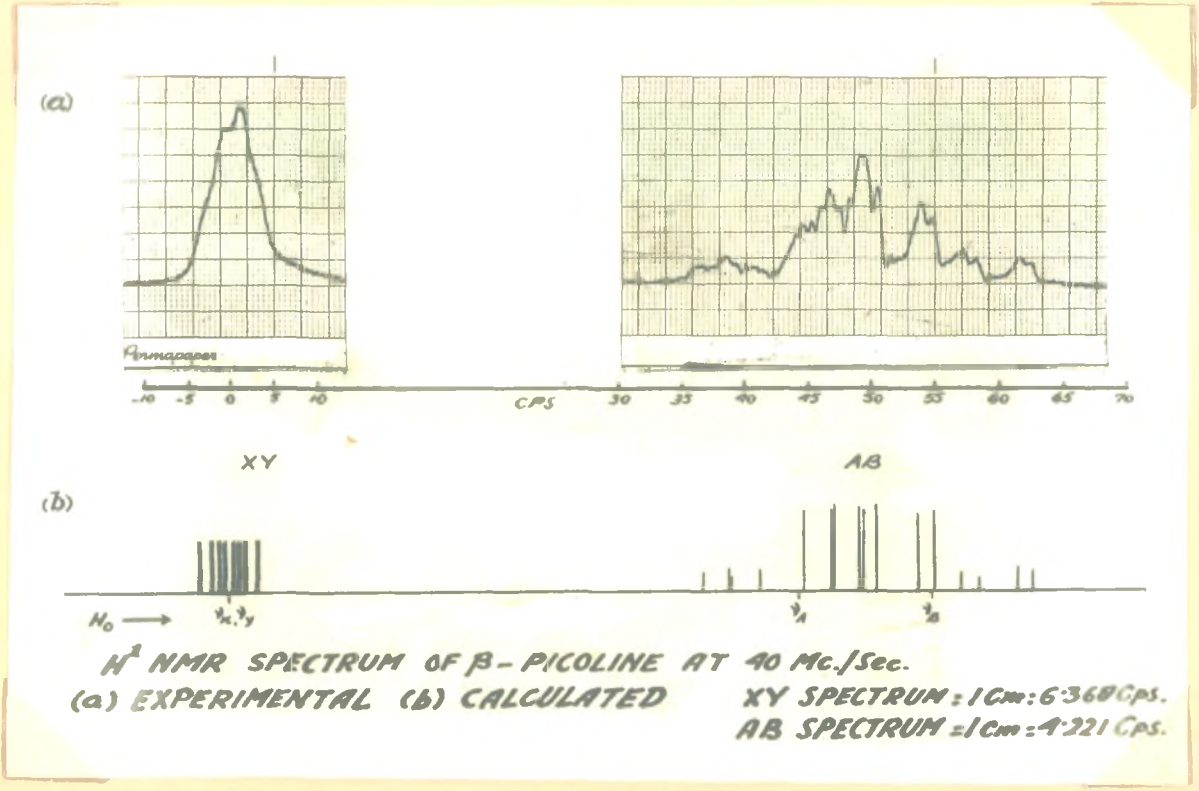
* See Figure IV.2.

transitions are obtained as given by (I.10). The mixed wave functions and the corresponding energy levels are given in Table IV.1.

The calculated transitions frequncies and relative intensities along with the observed frequencies are given in Table IV.2. The chemical shifts of the different protons in the molecule with respect to the signal from water are also given at the end of the Table IV.2. The calculated spectrum is shown in Fig. IV.1(b).

(iv) β-Picoline:

Fig. IV.3(a) shows the proton resonance spectrum of the ring protons of this molecule. The spectrum has two groups of lines and by a comparison with the spectra of pyridine and 3-pyridine-d_1, obtained by Schneider et.al (3), it is easy to see that the protons in 2 and 5 positions (Fig. IV.4) give rise to the lines at the lower field, while the lines at the higher field are due to the protons 3 and 4. As the separation between the centers of the two groups of lines is about 50 cps. and since any of the coupling constants between the nuclei belonging to the two groups is not expected to exceed about 6 cps. (by comparing with the corresponding parameters in pyridine (3)) the molecule can be taken to belong to the class ABXY (as shown in Fig.IV.4) in the usual notation.



H^1 NMR SPECTRUM OF β-PICOLINE AT 40 Mc./Sec.
(a) EXPERIMENTAL (b) CALCULATED

XY SPECTRUM = 1 Cm : 6·360 Cps.
AB SPECTRUM = 1 Cm : 4·221 Cps.

Fig. IV. 3.

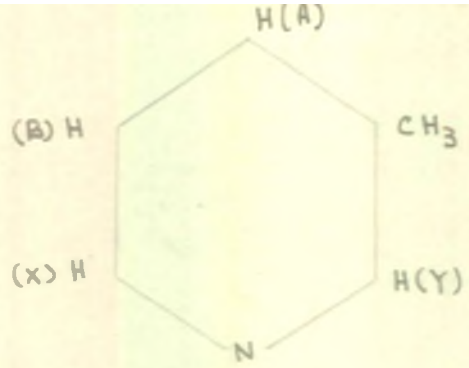


Fig IV.4

The zero order eigenfunctions and the corresponding diagonal matrix elements for ABXY system are the same as those for ABCX system in Table II.1 with C replaced by X, and X replaced by Y. The non-vanishing off-diagonal elements are given by the following relations:

$$\left.\begin{aligned} \mathcal{H}_{23} = \mathcal{H}_{79} = \mathcal{H}_{8,10} = \mathcal{H}_{14,15} = \tfrac{1}{2} J_{XY} \\ \mathcal{H}_{45} = \mathcal{H}_{78} = \mathcal{H}_{9,10} = \mathcal{H}_{12,13} = \tfrac{1}{2} J_{AB} \end{aligned}\right\} \quad \ldots \quad (\text{IV}.9)$$

and the remaining off-diagonal elements are obtained by the condition

$$\mathcal{H}_{mn} = \mathcal{H}_{nm} \quad \ldots \quad (\text{IV};10)$$

Now, the total spin matrix factors into four (1 x 1) (states 1,6,11 & 16), four 2 x 2 (states 2 & 3 and 4 & 5, and 12 & 13 and 14 & 15) and one 4 x 4 (states 7,8,9 & 10) submatrices. Explicit expressions are, therefore, directly obtained for all but four of the states.

The coupling constant in pyridine corresponding to J_{XY} is found to be 0.4 cps. (3). It can be seen from the group of lines assigned to X & Y that J_{XY} should be small. It is, therefore, assumed that $J_{XY} = 0$ to carry

out the analysis. The validity of this assumption can be judged from the extent to which the analysis satisfactorily accounts for the observed spectrum. Substituting $J_{XY} = 0$, the spin matrix can be completely solved, and explicit expressions can be derived for all the energy levels and the corresponding wave functions.

The problem now becomes exactly similar to that of 1-fluoro, 2,4-dinitrobenzene (Sec.II.iii). By replacing C by X, and X by Y and then substituting $J_{XY} = 0$ in Tables (II.2), (II.3), (II.4) & (II.5), the energy levels and wave functions, and the transition energies and their relative intensities involved in this problem are obtained.

Only the AB part of the spectrum can be analyzed in the present case, as the X and Y lines (on the lower field side in the observed spectrum) are not resolved. The theoretical AB spectrum consists of four quartets just as in the case of 1 fluoro, 2,4-dinitrobenzene spectrum (Sec.II.iv (c)), and the assignment of the lines to these quartets is to be done in a similar manner. From this assignment J_{AB}, $(\nu_A - \nu_B)$, $(J_{AX}-J_{BX})$ and $(J_{AY}-J_{BY})$ can be obtained. The centers of D_+, F_+, F_- and D_- quartets (see Sec.II.iv (c)) with respect to $\frac{1}{2}(\nu_A+\nu_B)$ are respectively given by

TABLE IV.3.

Calculated transition frequencies and relative intensities, and observed frequencies for β -picoline.

Transition No.†	Calculated frequency †† (in cps.)	Observed frequency # (in cps.)	Calculated Relative Intensity.
AB lines			
2	36.7	36.7	0.36
10	38.9	39.0	0.46
6	39.1		0.30
14	41.3	41.4	0.42
1	44.6	44.7	1.64
9	46.8	46.7	1.54
5	47.0		1.70
3	49.1	49.1	1.64
13	49.2		1.58
7	50.5	50.3	1.70
11	53.6	53.7	1.54
15	54.9	54.9	1.58
4	57.0	57.0	0.36
8	58.4	58.3	0.30
12	61.5	61.5	0.46
16	62.8	62.8	0.42

Contd..

TABLE IV.3 (Contd.)

Transition No.	Calculated frequency (in cps.)	Observed frequency (in cps.)	Calculated Relative Intensity.
X lines			
9	-13.6	—	0.0041
11	-12.5	—	0.0058
5	- 3.4	-3.1	1.0
8	- 3.4		1.0
2	- 1.2	-0.9	0.9959
6	- 1.1		0.9942
7	1.1	1.0	0.9942
3	1.2		0.9959
4	3.4	3.0	1.0
1	3.4		1.0
12	12.5	—	0.0058
10	13.6	—	0.0041
Y lines			
12	-14.2	—	0.0007
10	-11.9	—	0.0014
5	- 1.8	0.9	1.0
8	- 1.8		1.0
7	- 0.6		0.9993
4	- 0.5		0.9986

Contd..

TABLE IV.3 (Contd.)

Transition No.	Calculated frequency (in cps.)	Observed frequency (in cps.)	Calculated Relative Intensity.
3	0.5	1.0	0.9986
6	0.6		0.9993
2	1.8		1.0
1	1.8		1.0
9	11.9	—	0.0014
11	14.2	—	0.0007

† The transition Nos. for the AB, X and Y spectra are as in Tables II.3, II.4 and II.5 respectively, with C replaced by X, and X replaced by Y.

†† The calculated frequencies are given with respect to $\nu_x (= \nu_y)$ as the origin.

The observed frequencies are given with respect to the center of the XY group of lines. The standard deviations vary between 0.15 and 0.22cps.

Values of chemical shifts (δ) for the different protons with respect to the signal from water:— (The values are corrected for bulk diamagnetic susceptibility).

Type of proton *	δ w.r.t. H_2O in ppm
X, Y ..	-3.33±0.02
A ..	-2.22 "
B ..	-1.97 "
CH_3 ..	3.09 "

* See Figure IV.4.

As all the lines of both X and Y lie very close to each other within a small region, it is further assumed that $\delta_{XY} = 0^{*}$ to calculate the spectrum. The transition energies and their relative intensities calculated with the parameters in Eq. (IV.12) are given in Table (IV.3), along with the observed frequencies. The chemical shifts of the different protons in the molecule with respect to the signal from water are given at the end of the Table(IV.3). The calculated spectrum is shown in Fig. IV.3(b). The agreement between the observed and calculated spectra is satisfactory justifying the assumptions made in the analysis.

(v) γ-Picoline:

The ring proton spectrum of this molecule (Fig. IV. 5(a)) also shows two groups of lines separated by about 60 cps. Again by comparison with the spectra of pyridine and 4-pyridine-d_1 obtained by Schneider et.al., the group of lines at the lower field may be assigned to the protons ortho to N, (See figure IV. 6) while the other group may be assigned to the protons meta to N. As the separation between the two groups is much larger than any of the

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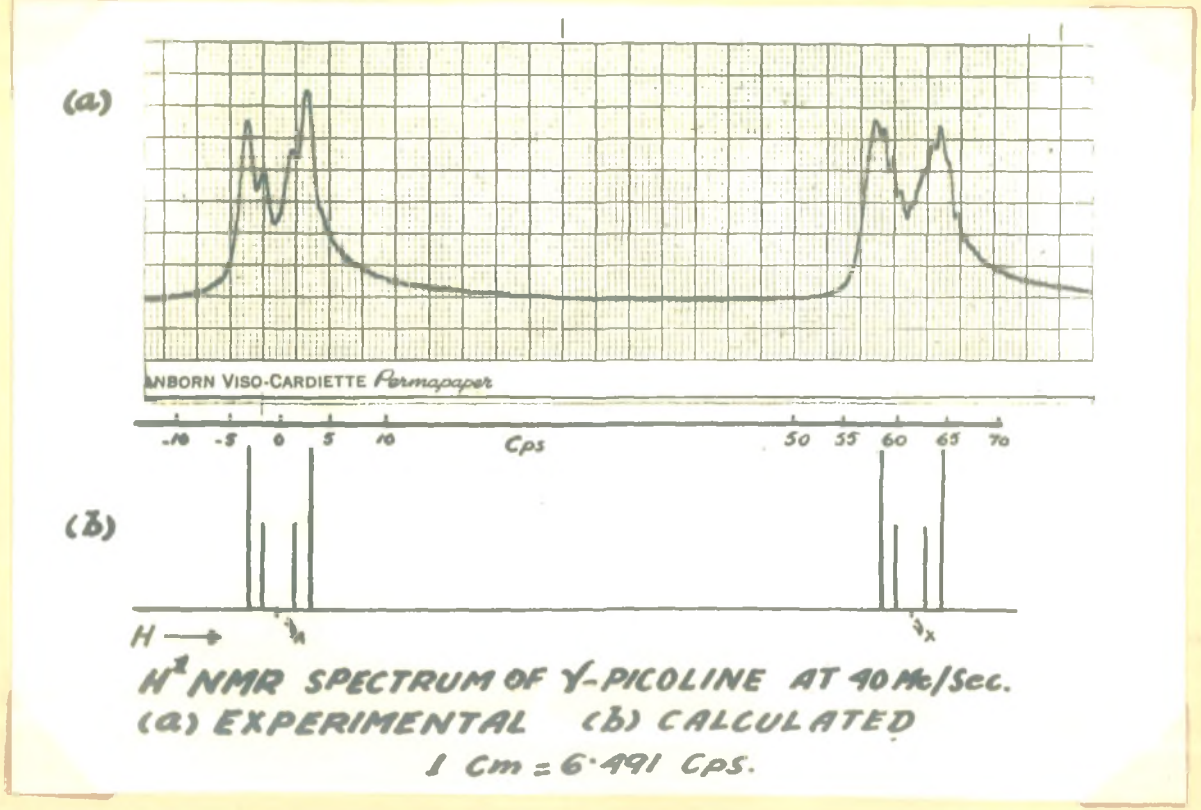
* When $\delta_{XY} = 0$ and $J_{XY} = 0$, the ABXY system may also be called as ABKK system.



H^1 NMR SPECTRUM OF γ-PICOLINE AT 40 Mc/Sec.
(a) EXPERIMENTAL (b) CALCULATED
1 Cm = 6·491 Cps.

Fig. IV. 5.

coupling constants involved, the spectrum may be taken to be of the A_2X_2 type. The general theory of this type of spectrum is given by several authors (6,7,8). In this spectrum the two groups of lines are completely identical in structure about their respective centers, and each group consists of twelve transitions. In the observed spectrum the lower field group of lines consists of four lines, while for the group at the higher field the structure appears to be a little complicated probably due to the coupling of these protons with the methyl protons. However, a general resemblance between the two groups can be seen.

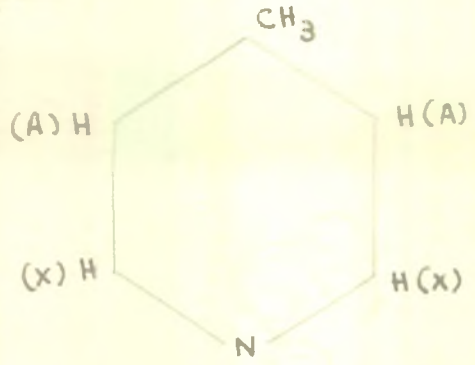


Fig IV.6

As the coupling between the two protons ortho to N is observed to be very small in pyridine, 4-pyridine-d_1 and β-picoline (see previous section), it may be taken as zero for the present analysis. The spectrum then belongs to the A_2X_2 class with K = M*. A typical half of such a

---

* K and M are defined as in Eq. (III.1) with B replaced by X. See also references (7 & 8).

spectrum consists of 6 transitions symmetrical with respect to the center as given by Bernstein et.al (7,8). The observed spectrum on the lower field side shows only four lines symmetrical with respect to the center. The other two lines (corresponding to transitions 5,8 and 9,12 as given in references 7 & 8) are comparatively weak and are expected to occur symmetrically on either side of the center, separated more than the lines at ± 3.1 cps. in the observed spectrum. As no absorption is indicated at these positions it is assumed that these lines coincide, within experimental error, with the strong lines at ± 3.1 cps. From the expressions for the transition energies and the mutual separations in the observed spectrum we then get*

$$\left.\begin{aligned} N &= 6.05 \text{ cps.} \qquad & K + \sqrt{K^2 + L^2} &= 6.05 \text{ cps.} \\ \sqrt{K^2 + L^2} - K &= 2.95 \text{ cps.} \end{aligned}\right\} \quad (\text{I V.13})$$

from which the coupling constants are obtained as

$$\left.\begin{aligned} J &= 5.1 \text{ cps.} \qquad & J_A &= 1.6 \text{ cps.} \\ J' &= 0.9 \text{ cps.} \qquad & J_X &= 0 \quad \text{cps.} \end{aligned}\right\} \quad (\text{IV.14})$$

The error involved in any of these values is not more than ± 0.4 cps.

The transition frequencies and the corresponding relative intensities for a typical half of the spectrum

---

* 6.05 represents an average of the mutual separations between the intense lines in the A_2 & the X_2 spectra. 2.95 represents the separation between the two inner components in the X_2 spectrum only as those in the A_2 spectrum are not easily identified.

TABLE IV.4.

Calculated transition frequencies and relative intensities, and observed frequencies for γ-picoline.

Transition No. †	Calculated frequency (in cps.)	Observed frequency (in cps.) ##	Calculated Relative Intensity.
1.	3.0		1.00
2	3.0	3.1	1.00
5	3.0		0.32
9	3.0		0.32
6	1.5	1.5	0.67
10	1.5		0.67
7	-1.5	-1.5	0.67
11	-1.5		0.67
3	-3.0		1.00
4	-3.0	-3.1	1.00
8	-3.0		0.32
12	-3.0		0.32

† The transitions represent a typical half of the spectrum. The transition Nos. are as in Table (6-18) of ref. 8 (P.141)

The error in the observed frequencies is about ± 0.2cps.

Chemical shifts (δ) in ppm with reference to water (corrected for bulk diamagnetic susceptibility):-

Type of Proton (See Fig IV.6)	δ
A	$\ldots -1.83 \pm 0.02$
X	$\cdots -3.37 \pm 0.02$

calculated with these parameters (Eq. (IV.14)) are given along with the observed frequencies ~~are given~~ in Table IV.4. The chemical shifts of the different protons with reference to signal of water, are given at the end of the Table IV.4. The calculated spectrum is shown in Fig. IV.5(b).

(vi) Discussion:

The coupling constants obtained from all these analyses do not differ in any striking manner from those in pyridine (5). This conforms to the general observation that π in coupling constants are not much sensitive to substitution.

The lines in all the three spectra are rather broad presumably due to quadrupole interactions arising because of the presence of nitrogen nucleus in the molecules, and due to the presence of slight traces of impurities in the samples used. The accuracy of the parameters is somewhat impaired due to this reason.

The chemical shift values also do not differ very much from those in pyridine showing that methyl substitution does not drastically alter the shielding of the ring protons in these molecules. The absolute chemical shifts, with reference to water, obtained here agree, within experimental errors, with the values obtained earlier at low resolution (1,2).

The calculated spectra in the case of β and γ picolines agree very satisfactorily with the observed spectra, as the analysis could be done in a direct manner. The agreement, however, is not completely satisfactory in the case of α-picoline as an approximate method involving many trial and error calculations had to be used in the analysis. The parameters obtained by Schneider et.al (3) for pyridine are of considerable help in carrying out the analyses of all the three spectra, particularly that of α-picoline.

REFERENCES.

1. Baker. E. B., J. Chem. Phys. 23, 1981 (1955).

2. Bernstein. H. J. and Schneider. W. G., J. Chem. Phys. 24, 469, (1956).

3. Schneider. W. G., Bernstein. H. J. and Pople. J. A., Ann. N. Y. Acad. Sci. 70, 806 (1958).

4. SripathiRao. H. (Private Communication).

5. Feesenden. R. W. and Waugh. J. S., J. Chem. Phys. 31, 996, (1959).

6. McConnell. H. M., McLean. A. D. and Reilly. C. A., J. Chem. Phys. 23, 1152, (1955).

7. Bernstein. H. J., Schneider. W. G., and Pople. J. A., Can. J. Chem. 35, 1060, (1957).

8. Pople. J. A., Schneider. W. G. and Bernstein. H. J., "High Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., Inc., New York, (1959).

CHAPTER V.

Cl^{35} RESONANCE SHIFTS IN AQUEOUS SOLUTIONS OF ALKALI CHLORIDES AND ALKALINE EARTH CHLORIDES, AND F^{19} RESONANCE SHIFTS IN SOME ALKALI FLUORIDES

Cl^{35} RESONANCE SHIFTS IN AQUEOUS SOLUTIONS OF ALKALI CHLORIDES AND ALKALINE EARTH CHLORIDES, AND F^{19} RESONANCE SHIFTS IN SOME ALKALI FLUORIDES.

A B S T R A C T.

The chemical shifts of Cl^{35} resonance in aqueous solutions of alkali chlorides and alkaline earth chlorides, and of F^{19} resonance in some alkali fluorides are determined at various concentrations using a High Resolution NMR Spectrometer. The shifts in alkali chlorides which are independent of concentration vary in the same manner as the quadrupole coupling constants in these molecules. These shifts probably represent the effect of the positive ions in these solutions. The F^{19} resonance shift in each alkali fluoride changes with concentration upto a certain limit after which it becomes practically constant. After such a limit the variation of these shifts from KF to CsF has the same trend as that for Cl^{35} resonance shifts from KCl to CsCl.

The Cl^{35} resonance shifts in alkaline earth chlorides are all found to be concentration dependent. This dependence is discussed in terms of the ion pair formation.

(i) Introduction:

Nuclear Magnetic Resonance technique was successfully employed by Shoolery and Alder (1) to understand some of the solvent ion interactions in aqueous electrolytes. They have investigated the proton resonance shifts in a large number of aqueous electrolytes and interpreted the data on the basis of the combined effect of polarization of the water molecules by the ions, and the tendency of these ions to rupture the hydrogen-bonded structure of water itself. In the same paper the concentration dependence of the F^{19}

resonance in aqueous solution of KF was reported. Later Carrington and Hines (2) have studied this concentration dependence in greater detail, using various solvents. These are the only cases, so far, to our knowledge, where negative ion shifts in aqueous electrolytes were studied.

In the present work the Cl^{35} resonance shifts are determined in aqueous solutions of alkali chlorides and alkaline earth chlorides at various concentrations. F^{19} resonance shifts in NaF, KF & CaF solutions were also determined. The NMR signals of Cl^{35} are, in general, broad (3) due to quadrupole interactions. Masuda (4) has determined the chemical shifts in four liquid chlorine compounds $TiCl_4$, $VOCl_3$, CrO_2Cl_2 and $SiCl_4$ and found the line widths to be proportional to the quadrupole coupling constants, showing that the quadrupole interactions form the dominant relaxation mechanism. But the line widths are less in the case of the highly ionised solutions studied here, where these interactions are comparatively low.

(ii) Experimental:

For Cl^{35} resonance experiments, the samples are contained in pyrex glass tubes of 13 mm o.d. The reference sample is placed in another glass tube of about 7 mm. o.d. and placed inside the main sample tube, so that the signals from the sample and reference are simultaneously observed.

The F^{19} resonance shifts are measured with samples contained in pyrex glass tubes of 9 mm o.d. The reference sample is contained in a thin glass tube of about 3 mm. o.d.

The signals obtained from RbCl with NaCl as the reference, along with the side bands separated by 184 cps., on either side from the two main signals are shown in Fig.V.1. Fig. V.2 shows the signals from LiCl & CsCl.

In the above mentioned form of the sample tubes, the sample will be contained in an annular space between the outer and inner tubes. Reilly, McConnell & Meisenheimer (5) have found that the annular samples give U-shaped doublets (broad line with two peaks), the separation being given by

$$\frac{\Delta H}{H_0} = 4\pi\left[(\chi_1 - \chi_2)\frac{a^2}{\gamma^2} + (\chi_2 - \chi_3)\frac{b^2}{\gamma^2}\right] \cdots \quad (V.1)$$

χ_1, χ_2 & χ_3 are the volume susceptibilities of the liquid in the inner glass tube, the glass tube, and the annular liquid respectively. γ refers to the mean radius of the annular liquid and a & b are the inner and outer radii of the inner glass tube. The signals obtained in the present case (Figs. V.1 and V.2) are not to be mistaken as such doublets, firstly because two signals are not obtained when the solution in the inner tube is not a chloride, and secondly the signal separations observed here are much larger than the separations which might be expected from annular samples on the basis of Eq.(V.1). However, in the case of F^{19} resonance in KF

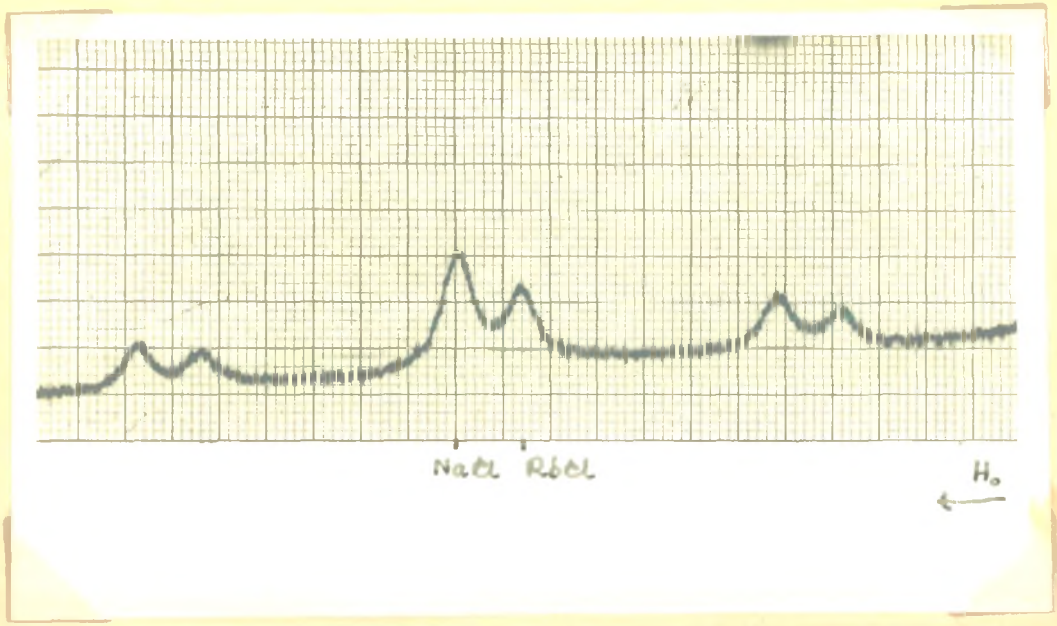


Fig. V. 1.

Cl^{35} NMR Signals from aqueous Solutions of RbCl and NaCl (reference) with Sidebands Separated by 184 Cps. on either Side of the main Signals.

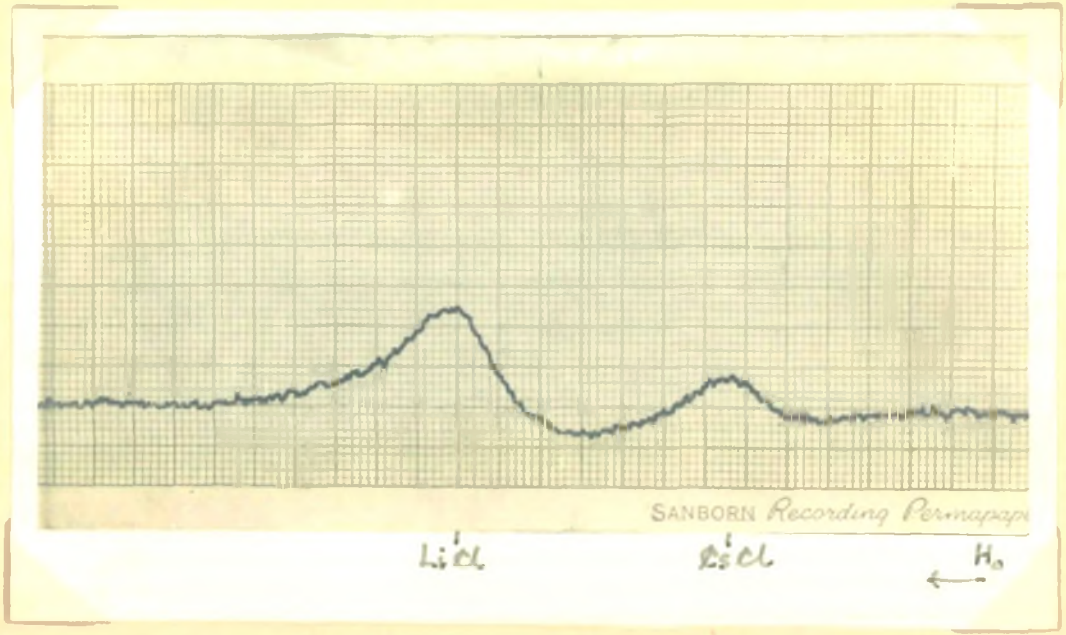


Fig. V.2.

Cl^{35} NMR Signals from LiCl and CsCl.

solutions such a splitting has been observed when a small glass tube, with or without any sample, is placed inside. Again it was not observed for CsF and NaF. The reason for observing it only in KF seems to be due to the fact that the line width in this case is much smaller than that for NaF or CsF, or any of the chloride solutions studied.

The chemical shift is given by

$$\delta = \frac{\nu_Y - \nu_C}{\nu_Y} \qquad \ldots \qquad (V.2)$$

and is expressed in parts per million (ppm). δ is here the chemical shift, ν_C and ν_Y are the Larmor frequency values for the nucleus under study in the compound and reference respectively. Though the experiment is actually done by varying the magnetic field and keeping the frequency constant, expressing δ in this form is convenient as the value of $(\nu_Y - \nu_C)$ is directly obtained in cycles per second from the measurement, when it is done by side-band technique.

The error involved in the measurement of Cl^{35} resonance shifts is about 1 ppm. For the F^{19} measurement it is about 0.1 ppm.

The results are not corrected for the bulk diamagnetic susceptibility. But this does not bring in any significant difference in the results, as the corrections involved are always within the experimental error given

above. Further, accurate data are not available to apply the correction for all the different concentrations of the solutions studied.

(iii) Results:

The Cl^{35} resonance shifts in alkali chlorides are given in Table V.1. These shifts are all found to be independent of concentration within the experimental error of 1.0 ppm. in the chemical shift. Therefore, an average value of the shifts obtained at the different concentrations is given. The values are all given with NaCl as the reference. The shifts in the case of LiCl and KCl are not measured with NaCl as the reference, but they were first measured with respect to CsCl and the values are finally reduced to NaCl as the reference. The error involved in these values may, therefore, be slightly more than 1.0 ppm.

The shifts in alkaline earth chlorides are all found to be concentration dependent. The values of these shifts at various concentrations for $BaCl_2$, $SrCl_2$, $CaCl_2$ and $MgCl_2$ are ~~all~~ given in Tables V.2(a), V.2(b), V.2(c) and V.2(d) respectively. The values are ~~all~~ given with reference to NaCl. In the case of $MgCl_2$ the measurement was not actually done with this reference as at low concentrations as there is considerable overlapping of the signals. The measurement was therefore done with reference to CsCl and later reduced to

TABLE V.1.

Sl. No.	Compound	Chemical shift δ in ppm.	Observed $eQq_{molecule}$ in Mc/Sec.	$(D-i)\beta\, eQq_{atom(14)}$ in Mc/Sec.
1.	LiCl	$-3.1 \pm 1.0^{*}$	..	..
2.	NaCl	0	<1	..
3.	KCl	$-1.8 \pm 1.0^{*}$	0.04	0.51
4.	RbCl	-10.5 ± 1.0	0.774	1.24
5.	CsCl	-23.2 ± 1.0	3.00	3.00

* The error in these cases may be slightly more (see text).

Variation of Cl^{35} resonance shifts with concentration in aqueous solutions of alkaline earth chlorides.

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(All the values given are with reference to NaCl. The error involved in the values is about $\pm$ 1.0 ppm.)

TABLE V.2(a)

$BaCl_2$

Serial No.	Molar Concentration	Chemical Shift in ppm.
1.	1.9	-11.6
2.	1.5	- 9.3
3.	1.3	- 7.6
4.	1.0	- 5.7

TABLE V.2(b)

$SrCl_2$

Serial No.	Molar Concentration	Chemical Shift in ppm.
1.	4.0	-14.7
2.	2.5	- 9.3
3.	1.7	- 6.2
4.	1.1	- 3.2

TABLE V.2(c)

$CaCl_2$

Serial No.	Molar Concentration	Chemical Shift in ppm.
1.	5.8	-19.0
2.	3.8	-11.1
3.	2.6	- 6.6
4.	2.2	- 5.1
5.	1.7	- 4.5

TABLE V.2(d)

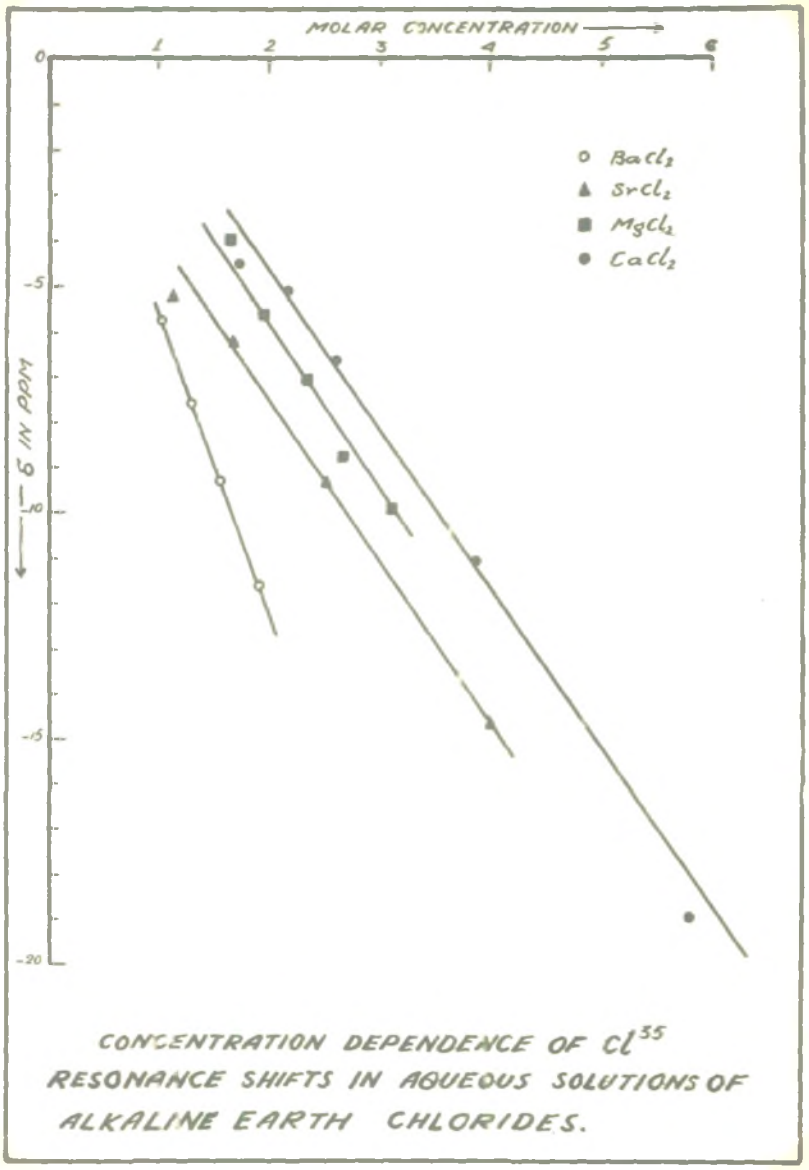
$MgCl_2$

Serial No.	Molar Concentration	Chemical Shift in ppm.
1.	3.1	- 9.9
2.	2.7	- 8.8
3.	2.3	- 7.0
4.	1.9	- 5.6
5.	1.6	- 4.0

NaCl as the reference. Once again this might increase the error involved in these measurements. The concentration dependence of these shifts in all the four compounds is plotted in Fig. V.3.

The F^{19} shifts in KF, NaF and CsF showed a concentration dependence at high concentrations. In KF solution the shielding of the F^{19} nucleus decreases with decreasing concentration, but after the concentration is about 8 M the shielding practically remains independent of further reduction in concentration. These results are in agreement with those of Shoolery and Alder (1) and a systematic measurement of the shifts at various concentrations is not undertaken. A similar behaviour is noted in the cases of CsF and NaF solutions. But the study could not be extended to lower concentrations as the signal intensity is feeble, in both these solutions. At the point when they become practically independent of concentration, the following values are obtained.

Compound.	δ in ppm.
NaF	0 (reference)
KF	-1.4 ± 0.2
CsF	-3.1 ± 0.2



CONCENTRATION DEPENDENCE OF Cl^{35} RESONANCE SHIFTS IN AQUEOUS SOLUTIONS OF ALKALINE EARTH CHLORIDES.

Fig. V. 3.

(iv) Discussion:

(a) Alkali chlorides & alkali fluorides:- Ramsey (6) has shown that the chemical shift arises due to the interaction between the molecular electrons and the external magnetic field. The interaction produces, in turn, a small magnetic field at the site of the nucleus in opposition to the external field. The magnitude of this shielding field is different, in different molecules due to variations in electronic structure.

If the alkali halides are 100% ionic, the shielding field for a particular halogen or alkali nucleus, according to Ramsey's theory, would not vary from molecule to molecule, and hence no shifts would be observed between these molecules. But several workers (7,8,9) have observed the chemical shifts in solid alkali halides both for alkali and halogen nuclear resonances. In all these cases (7,8,9) the observed shifts were explained by attributing a certain amount of covalent character to the crystalline bonds in these compounds. In the present work, the shifts are observed in aqueous solutions where crystalline fields are not expected. These shifts are much smaller in magnitude than those in the solid samples mentioned above.

Shoolery and Alder (1) pointed out from a consideration of electrostatic interactions only, that in cases

where ion pair formation or other interactions like covalent complex formation are not present, the shielding of the negative ion would increase with increasing concentration. This explains the shift of F^{19} resonance in K F, NaF & CsF to higher field as the concentration is increased (at high values of concentration only). Carrington and Hines, however, observed that this dependence might be explained otherwise also. In the case of alkali chlorides, the interactions proposed to explain the concentration dependence, are probably negligible, at least in the range of concentrations studied, (In these experiments the concentration has been decreased in steps from the saturation value to about ½ or 1/5th of it. This limit is usually set by the intensity of the resonance signal) as the shifts are found, within experimental errors, to be independent of concentration.

In a recent publication (10) we have pointed out a similarity of these shifts in alkali chlorides to the known quadrupole coupling constants of the chlorine atom in these molecules in gas phase. In general the similarity can be expected (4,11), as both these depend upon the fraction of unbalanced p-character about the atom in question. The quadrupole coupling constant for a halogen atom forming a hybrid bond, with a negative ionic character of amount β is given by (12)

$$e Q q_{molecule} = (-1 + \alpha - S^2)(1-\beta)\, e Q q_{atom} \quad \ldots \quad (V.3)$$

where α is the hybridization, S is the overlap factor and eQq_{atom} is known from atomic data (13). It can be seen from Eq. (V.3) that $eQq_{molecule}$ would be zero if the ionic character is 100% i.e $\beta = 1$. The observed values of the quadrupole coupling constants of K Cl, RbCl & CsCl, in the gaseous phase, were explained by Venkateswarlu and Jaseja (14) by modifying the above expression as

$$eQq_{molecule} = \left[(-1+\alpha-S^2)(1-\beta) + (D-i)\beta\right] eQq_{atom} \quad \cdots (V.4)$$

where D represents the effect on quadrupole coupling constant due to distortion of the closed shells of the halogen atom, and i represents the effect due to the presence of adjacent ions or atoms in the molecule. The observed values of $eQq_{molecule}$, and the contribution of the term $(D-i)\beta\, eQq_{atom}$ to these values, are given alongside with the experimental chemical shifts in Table V.1.

It may be noted that the chemical shift for LiCl with reference to NaCl is towards the same direction as that for KCl, RbCl & CsCl. For comparison of this behaviour, the quadrupole coupling constant is not known for LiCl, and it is not correctly found for NaCl. A similar behaviour can, however, be noted in the case of quadrupole coupling constants of bromine and iodine in the bromides and iodides of Lithium, sodium and potassium (14).

The aforementioned modification of the expression for $eQq_{molecule}$ essentially shows that the presence of the positive ion would slightly modify the electric field gradient at the site of the negative ion nucleus. However, these quadrupole coupling constants were observed in gas phase, whereas the shifts observed are in aqueous solutions. Here we cannot speak of a "bonding" as such between the two ions, but the positive ion may still be expected to make its presence felt by the negative ion, by forming a positive ion atmosphere around, even in the absence of any ion pair formation. The size of the positive ion increases as we go from Lithium to Cesium and therefore, the effect on the chlorine ion due to this positive ion atmosphere, can be expected to increase in the same order. The presence of a positive charge in the vicinity mainly draws the electrons away from the chlorine nucleus, thereby reducing the shielding. So the Cl^{35} resonance signal will be shifted to lower fields as we go from LiCl to CsCl, which accounts for the trend in the variation of the shifts in Table V.1, except for a change in the order in the case of LiCl. The same trend is observed in the case of fluorides, when they become independent of concentration. Even at higher concentrations the order is not changed.

It is probably not correct to assume that the above picture represents truely the many factors that contribute to changes in the shielding of the negative ion nucleus. The shielding is bound to be affected by the water molecules which are themselves polarized due to the presence of the ions. As discussed by Shoolery and Alder (1), the polarization of the water molecules decreases the shielding of protons while the breaking of the hydrogen bonds by the ions acts oppositely. The extent to which the solvent molecules affect the shielding of the ions, therefore depends on the relative contribution of these two effects, which in turn, depend on the solute molecules. Thus, it is difficult to disentangle these several factors and it can only be said that the overall effect on the shielding of the negative ion due to positive ions and water molecules in these solutions is such that the effect of the positive ion is more predominent. Further, there does not seem to be any obvious reason for the shifts in alkali chlorides to be concentration independent; but it appears that the variation, if any, is not large enough, in the range of concentration studied, to be observed outside the somewhat large experimental error involved.

(b) Alkaline Earth Chlorides:- The shifts in all the solutions studied are concentration dependent. In every case the shielding of the chlorine nucleus is found to increase with decreasing concentration. The plot of these variations for

the four cases in Fig. V.3 shows that the variation is roughly linear in every case.

As mentioned before, according to Shoolery and Alder (1), the shielding of the negative ion should increase with increasing concentration, unless ion pair formation or other interactions are present. If ion pair formation takes place the shielding will decrease, provided the positive ion polarises the negative ion more than the water molecule it displaces.* The ion pair formation is most probable at high concentrations and as the concentration decreases, the formation of these pairs is reduced.

If we assume that ion pairs are formed at high concentrations in these molecules and that the positive ions polarise the chlorine ion more than the water molecules, the increase in the shielding with decreasing concentration, observed in the present experiments is easily understood. The shielding observed is an average of the shielding experienced by the nucleus in different states** and it will be

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* Carrington and Hines (2) point out that it may be necessary to reconsider this, in view of the results obtained by Connick and Poulson (15) who found that AlF^{++} and AlF_2^{+} give resonances at higher field than the aqueous fluoride ion.

** This is due to the fact that rapid exchange of ions in different states takes place.

smaller at high concentrations because of the presence of larger number of ion pairs, than at lower concentrations, where the number of these pairs is reduced. It can be seen from Fig. V.3 that at the same concentration the shielding increases in the order $CaCl_2$, $MgCl_2$, $SrCl_2$ & $BaCl_2$. The electronegativity of the alkaline earth atoms decreases in the order Mg, Ca, Sr & Ba. Except for a change in the order in the case of $MgCl_2$, these results point out that the shielding increases as the electronegativity of the atom taking part in the ion pair formation is decreased. This seems to agree with the general observation that the shielding of the nucleus decreases as the electronegativity of the atom, directly bonded to the atom containing the nucleus of interest, increases. The same trend of variation in the shielding may also arise partly due to the increasing size of the positive ion as we go from Mg to Ba. (The order is changed in the case of $MgCl_2$) as in the case of the alkali chlorides discussed earlier.

In view of the fact that there is yet no unambiguous evidence regarding ion association, and as the effect of the solvent molecules on the shielding of the ions is not well understood, only general conclusions can be drawn from these results, and there does not seem to be any obvious inconsistency in the assumptions made above to explain the observed results. Further, difficulties arise in the present case as the accuracy is limited by the large line widths.

REFERENCES.

1. Shoolery. J. N. and Alder. B. J., J. Chem. Phys. 23, 805, (1955).

2. Carrington. A. and Hines. T., J. Chem. Phys. 28, 727, (1958).

3. Wertz. J. E., J. Chem. Phys. 24, 484, (1956).

4. Masuda. Y., J. Phys. Soc. Japan. 10, 85, (1955).

5. Reilly. C. A., McConnell. H.M. and Meisenheimer. R. G., Phys. Rev. 98, 264A (1955).

6. Ramsey. N. F., Phys. Rev. 78, 699, (1950).

7. Gutowsky. H. S. and McCarvey. B. R., J. Chem. Phys. 21, 1423, (1955).

8. Bloembergen. N. and Sorokin. P. P., Phys. Rev. 110, 865, (1958).

9. Kanda. T., J. Phys. Soc. Japan. 10, 85, (1955).

10. Venkateswarlu. P. and Nageswara Rao. B. D., Proc. Ind. Acad. Sci. 50A, 254, (1959).

11. Saika. A. and Slichter. C. P., J. Chem. Phys., 22, 26, (1954).

12. Dailey. B. P. and Townes. C. H., J. Chem. Phys., 23, 118, (1955).

13. Jaccarino, King and Stroke, (See reference 12).

14. Venkateswarlu. P. and Jaseja. T. S., Proc. Ind. Acad. Sci. 44A, 72, (1956).

15. Connick. R. E. and Poulson. R. E., J. Am. Chem. Soc. 79, 5153 (1957).